PHASE TRANSITION TEMPERATURES OF PSEUDOQUATERNARY Fe-C-Cr-O ALLOYS

Bedřich SMETANA [1,2], Ľubomíra DROZDOVÁ [1,2], Lenka ŘEHÁČKOVÁ [1,2], Vlastimil NOVÁK [1,2], Simona ZLÁ [1,2], Monika KAWULOKOVÁ [1,2], Andrew WATSON [3], Mario MACHŮ [1,2], Filip RADKOVSKÝ [1], Hana FRANCOVÁ [1], Petr KOZELSKÝ [1], Jana DOBROVSKÁ [1,2]

[1]*VSB - Technical University of Ostrava, Faculty of Metallurgy and Materials Engineering, Ostrava, Czech Republic, EU, bedrich.smetana@vsb.cz*

[2]*VŠB-Technical University of Ostrava, Regional materials science and technology centre, Ostrava, Czech Republic, EU, bedrich.smetana@vsb.cz*

[3]*Univ. Leeds, Sch. Chem. & Proc. Engn., Inst. Mat. Res., Leeds, W. Yorkshire, England, EU, andywatson7@gmail.com*

Abstract

The paper deals with the study of phase transition temperatures of pseudoquaternary Fe-C-Cr-O based alloys from RT up to 1600 °C. The knowledge of phase transition temperatures is crucial for application purpose and also for basic research related always closely to the applications. The deeper insight in to the knowledge of behavior of simple systems can lead to the enhancement of production of more complex alloys with enhanced properties by simultaneous lower cost production. The paper deals with phase transition temperatures such as: temperature of eutectoid transformation, magnetic transition, alfa-gama transition, solidus and liquidus temperature and peritectic transformation temperature. Phase transition temperatures were obtained by Differential Thermal Analysis (DTA). The comparison and discussion with calculated phase transition temperatures (IDS - Solidification Analysis Package, TC - Thermo-Calc) was done. In some cases substantial differences between experimental and calculated phase transition temperatures were encountered.

Keywords: Fe-C-Cr-O based alloys, phase transitions, temperatures, DTA

1. INTRODUCTION

It is necessary, for each steel production company, to improve and optimize production processes continuously to compare favourably with other competitors. The better control of the entire steel production cycle - from selection of quality raw materials, through proper control of primary and secondary metallurgy processes, and finally, the optimum setting of casting and solidification conditions, is necessary for modern competitive steel making company.

To improve and optimize the technological processes of steel production is it necessary to know, among others, the proper material data. One of many important data for steel production process are phase transition temperatures (from low and also high temperature region up to 1600 °C). In low temperature region are very important phase transition temperatures of e.g. eutectoid transformation, α - γ transition, temperature of Curie point etc. [1], which are important for subsequent heat and mechanical treatment. In the high temperature region are the most important temperatures of solidus and liquidus [2], which are important mainly for setting of casting conditions.

There are often used for predicting of phase transition temperatures for complex systems (steels) many relations and SWs [3]. It is possible to obtain very fast the results using calculating tools, but often can these data differ from the real state because of many simplifications and aproximations used and also the data in the used database(s) can be restricted. To obtain the most reliable data for more complex systems e.g. steels it is

necessary to have most proper data for lower order systems, e.g. in our case for pseudoquaternary Fe-C-Cr-O system (alloys). The results obtained with calculation relations and SWs are very often used for the subsequent simulations of real steel processing (heat treatment and casting) using e.g. SW PROCAST [4].

This paper presents results (phase transition temperatures from low and also high temperature region) obtained by DTA method [5] and SW calculations for three model Fe-C-Cr-O Alloys, with graded chromium content, prepared at our foundry laboratories. The changing chromium and oxygen content is investigated and discussed in this work. Experimentally obtained data were compared with results obtained using SW Thermo-Calc (TC SW. Ver. 2017a) and database TCFE8.

2. EXPERIMENT

Three model alloys (Cr 1, Cr 3 and Cr 5) were prepared at our working site in our foundry laboratories with specified composition, **Table 1**. Pure metals (Fe, Cr) and carbon was used for melting in induction vacuum furnace. Three kg ingots were cast and then cut and machined in to the sticks with a diameter 3.5 mm. For DTA Analysis were prepared cylinders about the height 2.5 mm. The sample mass was from 150 up to 200 mg. For each alloy were performed three runs at heating rate 10 °C·min^{-1} (three pieces of each alloy were analysed) in dynamic Ar (6N) atmosphere in corundum crucibles with lids.

Table 1 Chemical composition of analysed samples, wt. %, the content of other determined elements is lower than 0.005 wt. % (Ni, P, S, Si, Al, Cu, Ti, Mo, Co, V, B, H, Zr)

Sample	C	Cr	O	Mn	N	W
Cr 1	0.344	0.924	0.0021	0.056	0.026	0.025
Cr 3	0.342	2.970	0.0195	0.050	0.043	0.024
Cr 5	0.340	4.760	0.0015	0.042	0.001	0.044

3. CALCULATIONS

Theoretical calculations were performed using Thermodynamic SW Thermo-Calc [4]. Some simplifications of adopted models are presupposed for this SW and also the basis of data needed for calculations are limited. Thermo-Calc SW was used for calculation of phase transition temperatures, phase diagrams (for high temperature-HT-region) and property diagrams (for low temperature-LT-region). Only Fe, C and Cr were included for calculations of phase diagrams and property diagrams. Phase transition temperatures were also calculated with the widest possible composition (O, H, N, S and Zr not included, other elements presented in **Table 1** included: Ni, P, Si, Al, Cu, Ti, Mo, Co, V and B). Only BCC, FCC, CEMENTITE, M7C3, M3C2, M23C6 and LIQUID phase were considered for calculations

4. RESULTS AND DISCUSSION

Obtained DTA curves are presented at **Figures 1** and **2**. **Figure 1** presents DTA curves (in LT-region) also with marked phase transition temperatures: start of alfa gamma transition ($T_{\alpha\text{-}\gamma,S}$), Curie point tmperature (T_C) and end of alfa to gamma phase transition temperature ($T_{\alpha\text{-}\gamma,E}$). **Figure 2** presents DTA curves (in HT-region) also with marked phase transition temperatures: start of melting - solidus temperature (T or T_S), temperature of start of peritectic transition (T_P) and temperature of liquidus (T_L).

Experimental and calculated phase transition temperatures are included also in **Tables 2-7**. Mean values, standard deviations and variation coefficients were calculated for experimental results.

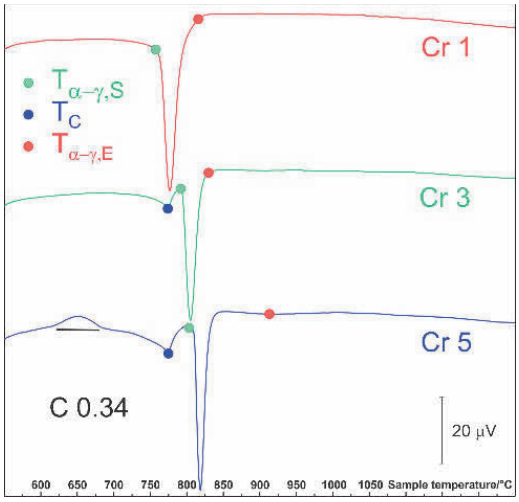

Figure 1 DTA curves of analysed samples Cr 1, Cr 3 and Cr 5 in low temperature (LT) region, $T_{\alpha-\gamma,S}$, T_C and $T_{\alpha-\gamma,E}$

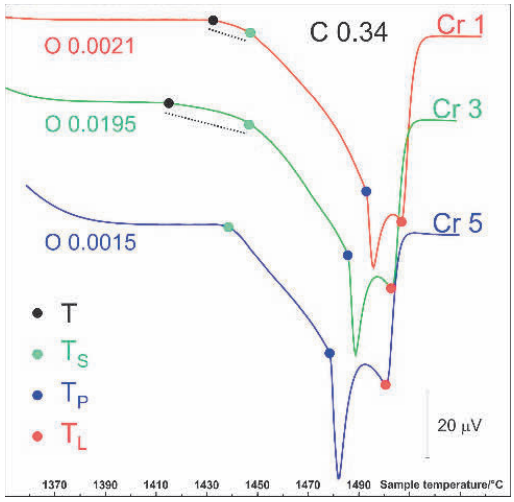

Figure 2 DTA curves of analysed samples Cr 1, Cr 3 and Cr 5 in high temperature (HT) region, T, T_S, T_P and T_L

Tables present also calculated values considering only three elements: Fe, C and Cr, ternary Alloys only, TC (Fe-C-Cr) and results considering elements as mentioned above (widest possible composition): TC (all). Experimentally obtained results are aslo compared with calculated cuts of ternary system Fe-C-Cr and ternary property diagrams, **Figures 3-8**.

Table 2 Phase transition temperatures in LT-region, alloy Cr 1

Analysis	$T_{\alpha->\gamma,S}$	T_C	$T_{\alpha->\gamma,E}$
	(°C)		
1	768	-	823
2	767	-	821
3	767	-	821
Mean value	**766**	**-**	**820**
Stand. Dev.	0	-	1
Var. coef. (%)	0.06	-	0.11
TC (Fe-C-Cr)	**744**	**-**	**793**
TC (all)	**744**	**-**	**794**

Table 3 Phase transition temperatures in HT-region, alloy Cr 1

Analysis	T	T_S	T_P	T_L
	(°C)			
1	1439	1458	1499	1504
2	1438	1453	1498	1504
3	1438	1452	1498	1503
Mean value	**1438**	**1454**	**1498**	**1504**
Stand. Dev.	0	3	0	0
Var. coef. (%)	0.03	0.18	0.03	0.03
TC (Fe-C-Cr)	-	**1411**	**1494**	**1509**
TC (all)	-	**1411**	**1495**	**1508**

Table 4 Phase transition temperatures in LT-region, alloy Cr 3

Analysis	$T_{\alpha->\gamma,S}$	T_C	$T_{\alpha->\gamma,E}$
	(°C)		
1	797	778	823
2	798	779	825
3	799	778	824
Mean value	**798**	**778**	**824**
Stand. Dev.	1	0	1
Var. coef. (%)	0.10	0.06	0.10
TC (Fe-C-Cr)	**775**	**765**	**826**
TC (all)	**774**	**765**	**793**

Table 5 Phase transition temperatures in HT-region, alloy Cr 3

Analysis	T	T_S	T_P	T_L
	(°C)			
1	1421	1452	1491	1500
2	1423	1459	1491	1500
3	1425	1458	1491	1500
Mean value	**1423**	**1456**	**1491**	**1500**
Stand. Dev.	2	3	0	0
Var. coef. (%)	0.11	0.21	0.00	0.00
TC (Fe-C-Cr)	-	**1464**	**1490**	**1506**
TC (all)	-	**1462**	**1489**	**1505**

Obtained DTA curves have classical shapes, only in the case of alloy Cr 5 it is visible small peak between 615-680 °C (black full strait line). It could correspond with decomposition of non-equilibrium phases in the sample [6]. The Curie point temperature was not determined at sample Cr 1 because of ovelapping of heat effects of alfa-gamma transformation and magnetic transition.

In the region of melting it was not possible unequivocally to determine solidus temperatures for samples Cr 1 and Cr 3 (see the region denoted by dotted line). The solidus temperature, with high probability, falls within the T and T_S temperatures (it needs to be investigated further to determine the true solidus temperature). It seems that with increasing oxygen content, with high probability, is widened the intrval between T and T_S and if the oxygene content is more substantially lowered (Cr 5 sample), the region between T and T_S is no more visible. This fact was observed in previous experimental studies [7], but i tis necessary to confirm this by further work.

Table 6 Phase transition temperatures in LT-region, alloy Cr 5

Analysis	$T_{\alpha\to\gamma,S}$	T_C	$T_{\alpha\to\gamma,E}$
	(°C)		
1	813	779	909
2	816	779	910
3	815	779	894
Mean value	**814**	**779**	**904**
Stand. Dev.	1	0	7
Var. coef. (%)	0.15	0.00	0.81
TC (Fe-C-Cr)	**801**	**777**	**894**
TC (all)	**800**	**777**	**804**

Table 7 Phase transition temperatures in HT-region, alloy Cr 5

Analysis	T_S	T_P	T_L
	(°C)		
1	1444	1484	1498
2	1444	1484	1498
3	1443	1484	1498
Mean value	**1444**	**1484**	**1498**
Stand. Dev.	0	0	0
Var. coef. (%)	0.03	0.00	0.00
TC (Fe-C-Cr)	**1462**	**1482**	**1502**
TC (all)	**1460**	**1481**	**1502**

Comparing the calculated values TC (Fe-C-Cr) and TC (all) the relativelly small deviations were encountered but not in the case of end of alfa gamma transition, the diference was even 33 °C in the case of sample Cr 3 and 11 °C in the case of sample Cr 5 (there are no higher differences than 2 °C in the case of other phase transition temperatures).

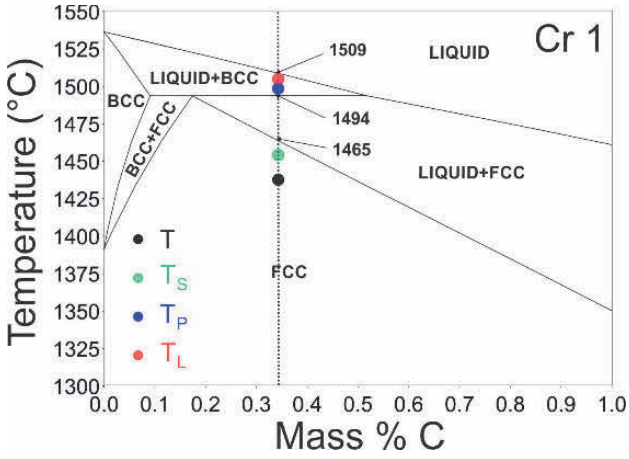

Figure 3 Comparison of isoplethal cut of ternary system Fe-C-Cr (composition according to the Table 1, Cr 1) and experimental temperatures obtained for alloy Cr 1: T, T_S, T_P and T_L

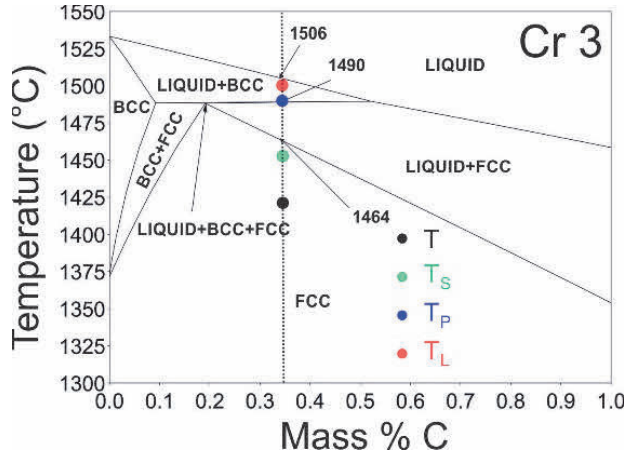

Figure 4 Comparison of isoplethal cut of ternary system Fe-C-Cr (composition according to the Table 1, Cr 3) and experimental temperatures obtained for alloy Cr 3: T, T_S, T_P and T_L

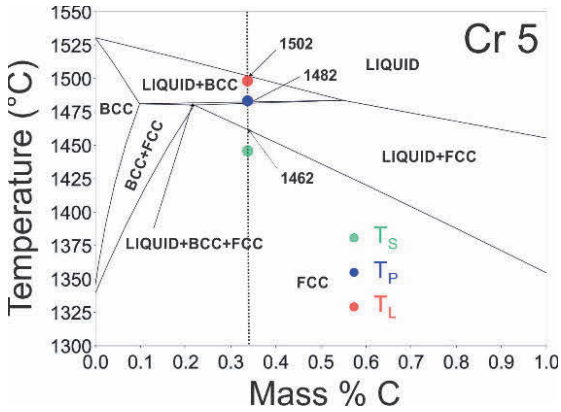

Figure 5 Comparison of isoplethal cut of ternary system Fe-C-Cr (composition according to the Table 1, Cr 5) and experimental temperatures obtained for alloy Cr 5: T_S, $T_{P\ and}$ T_L

To see the shift of phase transition temperatures more clear and their comparison with calculated data see also **Figures 3-8**. The differences between experimentally determined $T_{\alpha-\gamma,S}$ and theoretical values were within an interval 13-24 °C, in the case of Curie temperature were the differences 13 or 2 °C. The most pronounced dfifferences were encountered for $T_{\alpha-\gamma,E}$, see comparison of experimental and theoretical values and compare experimental values with calculated: TC (Fe-C-Cr) and TC (all); difference from 2 up to 100 °C. These differences have to be clarified in the future work by performing of structural and phase analysis.

Calculated and experimental values of $T_{P\ and}$ T_L differ only very slightly. The maximum difference is no more than 6 °C. But in the case of solidus temperatures the higher differences were obtained - up to 41 °C. But it can be stated also, that in the case of alloy Cr 1 and Cr 3 that was not unequivocal possible to determine the solidus temperature. The solidus temperature could be somewhere between, with high probability, $T_{\ and}$ T_S, see **Tables 3**, **5 and 7**.

The chromium content influence was observed, as published earlier [8-10]. It is possible to conclude that Cr increase the temperature of alfa-gamma start and end of this transition. In the case of Curie point temperature is the influence negligible. Liquidus temperature and temperature of start of peritectic transformation were also lowered with increasing Cr content. More pronounced lowering of temperature (shift to the lower temperature) was observed in the case of peritectic transformation temperature (approximately twice higher impact of Cr than in the case of liquidus temperature).

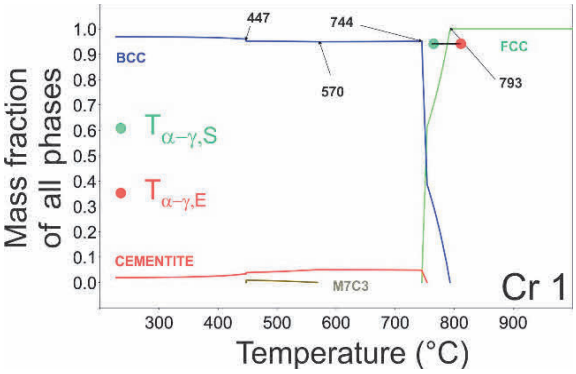

Figure 6 Comparison of property diagram of Fe-C-Cr ternary alloy (composition according to the Table 1, Cr 1) and experimental temperatures obtained for alloy Cr 1: $T_{\alpha-\gamma,S}$, and $T_{\alpha-\gamma,E}$

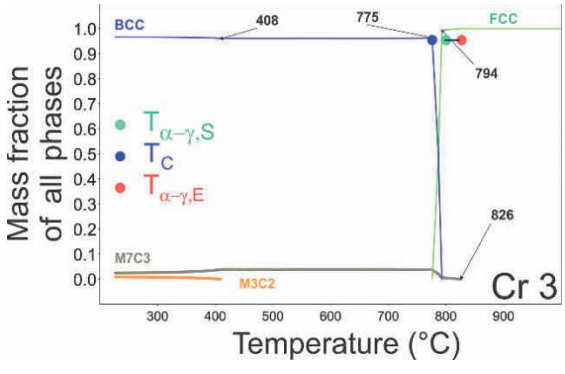

Figure 7 Comparison of property diagram of Fe-C-Cr ternary alloy (composition according to the Table 1, Cr 3) and experimental temperatures obtained for alloy Cr 1: $T_{\alpha-\gamma,S}$, T_C and $T_{\alpha-\gamma,E}$

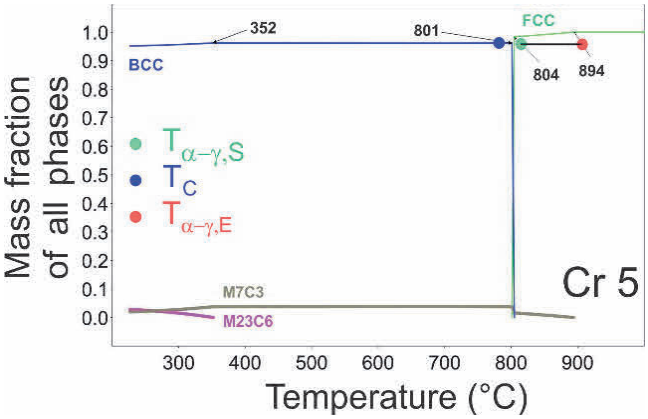

Figure 8 Comparison of property diagram of Fe-C-Cr ternary alloy (composition according to the Table 1, Cr 5) and experimental temperatures obtained for alloy Cr 1: $T_{\alpha-\gamma,S}$, T_C and $T_{\alpha-\gamma,E}$

5. CONCLUSION

Results obtained in this work showed the necessity, in some cases, to perform futrther experimental research in the field of phase transition temperatures concerning Fe-C-Cr-O based Alloys. Especially in the case of eutectoid transformation (start of alfa-gamma transition), end of alfa-gamma transition and solidus temperature. The differences between experimental and theoretical values are in some cases in tens of degrees of Celsius. Also the study of influence of oxygen content is planned in the future work. The chromium content influence, by constant carbon content, was investigated also and corresponding shifts of phase transition temperatures were observed, e.g. the influence of chromium content on shift of peritectic transformation temperatur is as twice higher than the influence on the liquidus temperature.

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