

TEMPERATURES OF PHASE TRANSFORMATIONS OF FE-C BASED ALLOYS

KALUP Aleš^{1,2}, DROZDOVÁ, Ľubomíra¹, ZLÁ Simona^{1,2}, KAWULOKOVÁ Monika^{1,2},
STROUHALOVÁ Michaela^{1,2}, DOBROVSKÁ Jana^{1,2}, SMETANA Bedřich^{1,2}

¹ Faculty of Metallurgy and Materials Engineering, VSB - Technical University of Ostrava, Ostrava, Czech Republic, EU, ales.kalup@vsb.cz

² Regional material science and technology centre, VSB - Technical University of Ostrava, Ostrava, Czech Republic, EU, bedrich.smetana@vsb.cz

Abstract

Experimental and theoretical investigation of temperatures of phase transformations (temperature of liquidus T_L , temperature of peritectic transformation T_P , temperature of solidus T_S , temperature of the end of $\alpha \rightarrow \gamma$ transformation Ac_3 , and temperature of the start of eutectoid transformation Ac_1) of these alloys were experimentally measured. All investigated temperatures were also calculated by Thermo-Calc software.

Comparison of measured and calculated temperatures of phase transformations was performed and good agreement was found for temperatures of liquidus and solidus. Discussion of identified differences between measured and calculated temperatures was also done.

Keywords: Temperature of phase transformation, melting, $\alpha \rightarrow \gamma$ transformation, Fe-C alloy, Thermo-Calc

1. INTRODUCTION

It is well-known, that chromium has significant effect onto properties of Fe-C based alloys/steels [1, 2]. Temperature of liquidus T_L decreases with increasing amount of Cr [3] while temperature of solidus slightly decrease with increasing amount of Cr [4]. Chromium also has influence on the stability of retained austenite [5] and formation of intermetallic phases [6], so temperatures connected with $\alpha \rightarrow \gamma$ transformation have to be also affected by this element.

Investigated quantities can be measured using thermal analysis methods. One of the most commonly used methods is Differential thermal analysis (DTA) [8]. Another commonly used method is Differential scanning calorimetry (DSC) [9].

Properties of Fe-C alloys/steels are nowadays often calculated using different software (i.e. Thermo-Calc [10], FactSage [11], CompuTherm [12]). Quality of theoretical results often depends on the settings of calculations [13], so for the best quality of theoretical calculations is necessary to use all the possibilities of the software settings.

In this paper, the DTA method was used for investigation of temperature of liquidus T_L , temperature of peritectic transformation T_P , temperature of solidus T_S , temperature of the end of $\alpha \rightarrow \gamma$ transformation Ac_3 and temperature of the start of eutectoid transformation Ac_1 . All temperatures were also calculated using Thermo-Calc software with TCFE8 (Thermo-Calc Fe-based alloys) database.

2. EXPERIMENTAL

Chemical composition of investigated Fe-C based alloys is in **Table 1**. Samples were ground up and washed in acetone under ultrasound before measurement. Measurements were done under inert atmosphere of pure argon (6N). All experimental values in this paper were obtained from heating runs and all experimental measurements were done three times for statistical purpose.

Table 1 Chemical composition of Fe-C based alloys (wt. %)

Sample	C	Cr	Mn	Si	S	Cu	Ni
1	0.270	0.738	1.148	0.233	0.004	0.075	0.032
2	0.284	0.614	0.790	0.208	0.009	0.068	0.029
3	0.252	0.940	0.360	0.295	0.002	0.070	0.030

Temperatures of phase transformations were measured using the Setaram SETSYS 18™ device (**Figure 1**). Heating rate was set to 10 °C·min⁻¹ for measurements in high-temperature area (temperatures of liquidus T_L , peritectic transformation T_P and solidus T_S).



Figure 1 Setaram SETSYS 18™ device.

For low-temperature area (temperatures of the end of $\alpha \rightarrow \gamma$ transformation A_{c3} , and temperature of the start of eutectoid transformation A_{c1}) was heating rate set to 5 °C·min⁻¹. Temperature calibration was made using pure metals (Pd and Al). Temperature of liquidus T_L was also calibrated to experimental conditions (i.e. sample mass, heating rate) according to [14].

3. CALCULATIONS

Calculations were performed using the Thermo-Calc software with TCFE8 (Thermo-Calc Fe-based alloys) database [15]. This software based on the CALPHAD approach allows many settings of calculations. In this paper, full chemical composition and all phases (except for graphite and diamond) were allowed.

4. RESULTS AND DISCUSSION

4.1. Melting area

All three temperatures of phase transformations in the melting area (T_L , T_P and T_S) decrease with increasing amount of Cr [16]. Temperatures of liquidus T_L and solidus T_S also decrease with increasing amount of Mn [17]. Moreover, temperatures of liquidus and solidus decrease with increasing amount of carbon [18].

Table 2 shows experimentally and theoretically obtained temperatures of phase transformations in the melting area (temperature of liquidus T_L , temperature of peritectic transformation T_P and temperature of solidus T_S) for all three investigated samples.

Table 2 Temperatures of liquidus T_L , peritectic transformation T_P and solidus T_S (°C)

Sample	T_L		T_P		T_S	
	Experimental	Calculated	Experimental	Calculated	Experimental	Calculated
1	1500 ± 1	1506	1491 ± 1	1487	1446 ± 5	1456
2	1500 ± 1	1506	1491 ± 1	1488	1449 ± 4	1447
3	1506 ± 4	1508	1476 ± 6	1477	1464 ± 5	1435

Calculated temperatures of liquidus T_L are in very good agreement with experimental values; difference is up to 6 °C for all three samples. Samples 1 and 2 have same experimental T_L (1500 ± 1 °C) and Thermo-Calc also calculated same value of T_L (1506 °C). Sample 3 has a little bit higher experimental T_L than for samples 1 and 2 and calculated T_L is a bit lower than for samples 1 and 2, too.

Samples 1 and 2 have same experimental T_P (1491 ± 1 °C), but sample 3 has significantly lower experimental T_P (1476 ± 0 °C). Sample 3 has higher amount of Cr (0.94 wt. %) than samples 1 and 2 (0.738 wt. % and 0.614 wt. %, respectively), so this should be the cause of lower values of T_P . Calculated values of T_P of all three investigated samples are in very good agreement with experimental values of T_P , difference is up to 4 °C.

Experimental and calculated T_S are in good agreement for samples 1 and 2 (difference is up to 10 °C). For sample 3, calculated temperature of solidus is 29 °C lower than measured value. This could be caused by the highest amount of Cr and/or the lowest amount of Mn.

4.2. Area of $\alpha \rightarrow \gamma$ transformation

Both investigated temperatures (Ac_3 and Ac_1) decrease with the amounts of Cr [19] and also Mn [20]. According to obtained (experimental and theoretical) values of Ac_3 and Ac_1 , it looks like the amount of Mn has higher impact on the shift of both temperatures than the amount of Cr.

Table 3 shows calculated and measured temperatures of phase transformations in the area of $\alpha \rightarrow \gamma$ transformation (Ac_3 and Ac_1) of all three investigated samples.

Table 3 Temperature of the end of $\alpha \rightarrow \gamma$ transformation Ac_3 , and temperature of the start of eutectoid transformation Ac_1 (°C)

Sample	Ac_3		Ac_1	
	Experimental	Calculated	Experimental	Calculated
1	813 ± 1	793	756 ± 0	710
2	811 ± 1	800	748 ± 0	720
3	849 ± 1	832	776 ± 1	744

All calculated values of Ac_3 and Ac_1 temperatures are lower than corresponding experimental values. The difference between measured and calculated values of Ac_3 is cca 15 °C and the difference between measured and calculated values of Ac_1 is cca 30 °C

This could be caused by the calculations in the equilibrium state (Thermo-Calc does not allow calculations in non-equilibrium state). All phases (except for graphite and diamond) were allowed for calculations, so it is

possible, that samples contain different minor phase (phases) than those determined by Thermo-Calc software (i.e. $M_{23}C_6$, M_7C_3).

Experimental values of Ac_1 were set to extrapolated onset of peak and this onset depends on the heating rate [21], so this should be also one of the reasons for lower agreement between experimental and theoretical values of Ac_1 .

5. CONCLUSIONS

All calculated temperatures of phase transformations in the melting area (temperature of liquidus T_L , temperature of peritectic transformation T_P and temperature of solidus T_S) are in very good agreement with measured values, except for one value of T_S . Difference between values is up to 6 °C for temperatures of liquidus, 4 °C for temperatures of peritectic transformation and 10 °C (respective 29 °C) for temperatures of solidus.

Calculated temperatures of phase transformation in the area of $\alpha \rightarrow \gamma$ transformation (temperature of the end of $\alpha \rightarrow \gamma$ transformation Ac_3 and temperature of the start of eutectoid transformation Ac_1) are significantly lower than experimental values. Calculated temperatures Ac_3 are 11-20 °C below experimental values and calculated temperatures Ac_1 are 28-46 °C below experimental values.

Based on the performed experiments, it appears that Mn has higher influence on all investigated temperatures of phase transformation (T_L , T_P , T_S , Ac_3 and Ac_1) than Cr.

ACKNOWLEDGEMENT

This paper was created on the Faculty of Metallurgy and Materials Engineering in the Project No. LO1203 "Regional Materials Science and Technology Centre - Feasibility Program" funded by Ministry of Education, Youth and Sports of the Czech Republic, GAČR project No. 17-18668S and student project SP2017/59.

REFERENCES

- [1] MEIER, G. H., JUNG, K., MU, N., YAMAR, N. M., PETTIT, F. S., ABELLÁN, J. P., OLSZEWSKI, T., HIERRO, L. N., QUADAKKERS, W. J., HOLCOMB, G. R. Effect of alloy composition and exposure conditions on the selective oxidation behavior of ferritic Fe-Cr and Fe-Cr-X alloys. *Oxidation on metals*, 2010, vol. 74, pp. 319-340.
- [2] MULFORD, R. A., McMAHON, C. J., POPE, D. P., FENG, H. C. Temper embrittlement of Ni-Cr steel by antimony: III. Effects of Ni and Cr. *Metallurgical transactions A*, 1976, vol. 7A, pp. 1269-1274.
- [3] FUKUMOTO, S., KURZ, W. The δ to γ transition in Fe-Cr-Ni alloys during laser treatment. *ISIJ International*, 1997, vol. 37, pp. 677-684.
- [4] THORPE, W., CHICCO, B. The Fe-rich corner of the metastable C-Cr-Fe liquidus surface. *Metallurgical transactions A*, 1985, vol. 16A, pp. 1541-1549.
- [5] HOSSAIN, R., PAHLEVANI, F., SAHAJWALLA, V. Effect of small addition of Cr on stability of retained austenite in high carbon steel. *Materials characterization*, 2017, vol. 125, pp. 114-122.
- [6] CHENG, W., WANG, Ch. Effect of chromium on the formation of intermetallic phases in hot-dipped aluminide Cr-Mo steels. *Applied surface science*, 2013, vol. 277, pp.139-145.
- [7] KHVAN, A. V., HALLSTEDT, B., BROECKMANN, Ch. A thermodynamic evaluation of the Fe-Cr-C system. *Calphad*, 2014, vol. 46, pp. 24-33.
- [8] KAWULOKOVÁ, M., SMETANA, B., ZLÁ, S., KALUP, A., MAZANCOVÁ, E., VÁŇOVÁ, P., KAWULOK, P., DOBROVSKÁ, J., ROSYPALOVÁ, S. Study of equilibrium and nonequilibrium phase transformations temperatures of steel by thermal analysis methods. *Journal of thermal analysis and calorimetry*, 2017vol. 127, pp. 423-429.
- [9] WILTHAN B., RESCHAB, H., TANZER, R., SCHÜTZENHÖFER, W., POTTLACHER, G. Thermophysical properties of a chromium-nickel-molybdenum steel in the solid and liquid phases. *International journal of thermophysics*, 2008, vol. 29, pp. 434-444.

- [10] HOMOLOVÁ, V., JANOVEC, J., KROUPA, A. Experimental and thermodynamic studies of phase transformations in Cr-V low alloy steels. *Materials and science engineering A*, 2002, vol. 335, pp. 209-297.
- [11] MALFLIET, A., CAMPFORTS, M., BLANPAIN, B. Influence of Cr and Ni content in stainless steel on the degradation mechanisms in PbO-CaO-SiO₂ slag. *Corrosion science*, 2012, vol. 57, pp. 1-10.
- [12] SMETANA, B., ŽALUDOVÁ, M., TKADLEČKOVÁ, M., DOBROVSKÁ, J., ZLÁ, S., GRYC, K., KLUS, P., MICHÁLEK, K., MACHOVČÁK, P., ŘEHÁČKOVÁ, L. Experimental verification of hematite ingot mould heat capacity and its direct utilisation in simulation of casting process. *Journal of thermal analysis and calorimetry*, 2013, vol. 112, pp. 473-480.
- [13] TKADLEČKOVÁ, M., MACHOVČÁK, P., GRYC, K., MICHÁLEK, K., SOCHA, L., KLUS, P. Numerical modelling of macrosegregation in heavy steel ingot. *Archives of metallurgy and materials*, 2013, vol. 58, pp. 171-177.
- [14] KALUP, A., SMETANA, B., KAWULOKOVÁ, M., ZLÁ, S., FRANCOVÁ, H., DOSTÁL, P., WALOSZKOVÁ, K., WALOSZKOVÁ, L., DOBROVSKÁ, J. Liquidus and solidus temperatures and latent heats of melting of steels. *Journal of thermal analysis and calorimetry*, 2017, vol. 127, pp. 123-128.
- [15] Thermo-Calc Software TCFE8 Steels/Fe-alloys database version 8 (accessed 23 July 2016)
- [16] KUNDRAT, K. M., CHOCHOL, M., ELLIOTT, J. F. Phase relationships in the Fe-Cr-C system at solidification temperatures. *Metallurgical transactions B*, 1984, vol. 15B, pp. 663-676.
- [17] LIU, X. J., HAO, S. M., XU, L. Y., GUO, Y. F., CHEN, H. Experimental study of the phase equilibria in the Fe-Mn-Al system. *Metallurgical and materials transactions A*, 1996, vol. 27A, pp. 2429-2435.
- [18] SUGDEN, A. A. B., BHADESHIA, H. K. D. H. Thermodynamic estimation of liquidus, solidus, A_{e3} temperatures, and phase compositions for low alloy multicomponent steels. *Materials science and technology*, 1989, vol. 5, pp. 977-984.
- [19] KIRCHNER, G., NISHIZAWA, T., UHRENIUS, B. The distribution of chromium between ferrite and austenite and the thermodynamics of the α/γ equilibrium in the Fe-Cr and Fe-Mn Systems. *Metallurgical and materials transactions*, 1973, vol. 4, pp. 167-174.
- [20] HILLERT, M., WALDENSTRÖM, M. A thermodynamic analysis of the Fe-Mn-C system. *Metallurgical transactions A*, 1977, vol. 8A, pp. 5-13.
- [21] KRIELAART, G. P., van der ZWAAG, S. Kinetics of $\gamma \rightarrow \alpha$ phase transformation in Fe-Mn alloys containing low manganese. *Materials science and technology*, 1998, vol. 14, pp. 10-18.