EXPERIMENTAL AND THEORETICAL DETERMINATION OF HEAT CAPACITIES OF MODEL ALLOYS BASED ON Fe-C-Cr

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Abstract

Three model alloys based on Fe-C-Cr were studied. Alloys contained carbon of 0.34 wt% and chromium in a range of 0.92 - 4.76 wt%. Heat capacities were studied in a low and high-temperature region. The experimental heat capacities ("apparent heat capacities") were obtained using Differential Scanning Calorimetry (DSC) with use of a continuous method. The Setaram MHTC (Multi High-Temperature Calorimeter) 96 with a3D DSC sensor was used for experiments with the use of the DSC method. Measurements were done in an inert atmosphere of pure argon by a heating rate of 5°C/min. The experimental data were compared and discussed with the calculation results using SW Thermo-Calc with the use of the TCFE8.1 (Thermo-Calc Fe-based alloys) database. Structural and phase analysis was performed with the use of the Olympus IX70 optical microscope. There is not an unequivocal trend in increase or decrease of experimental heat capacities with increasing content of chromium in the temperature range of 457.15 - 1370.15 K. Experimentally obtained heat capacities decrease with increasing content of chromium except for phase transformations in the temperature range of 1371.15 - 1853.15 K.

Keywords: Fe-C-Cr alloys, DSC, heat capacity, Thermo-Calc

1. INTRODUCTION

Thermophysical and thermodynamic properties of systems based on Fe were and still are a subject of extensive research [1-5]. To predict thermophysical and thermodynamic material properties of complex systems, it is necessary to have a high quality of experimental data of simpler systems such as Fe-C-O or Fe-C-O-Cr [1,2,6-8]. The key material data required for the thermodynamic and thermophysical description of materials include the heat capacities, the phase transformation temperatures, latent heat and others [2,4,9].

Heat capacities of steels are one of the crucial thermophysical parameters used for process behaviour prediction in many applications. Heat capacity is an input variable for many thermodynamical and kinetic programs. The dependences of heat capacity on common variables (temperature, pressure) are also commonly used as the input data in software packages (e.g. ProCast, Magmasoft, ANSYS Fluent) that are applicable in the field of applied research for simulations of technological processes. Experimental data of the heat capacities can be found in literature, but it is difficult to find data for given steel and alloys based on Fe (with exact chemical composition) [2,9].

To obtain thermophysical and thermodynamic properties, thermal analysis methods [10] are often used. This paper presents results obtained by one of the thermal analysis methods: Differential Scanning Calorimetry (DSC). By this method, heat capacities during continuous linear heating or cooling in the controlled atmosphere are studied. The heat flux of the analyzed sample is measured relative to the heat flux of the reference sample [10].

Experimentally, there were obtained heat capacities. These data were discussed and compared with results calculated using SW Thermo-Calc (ver. 2017a) and the TCFE8 database.

2. EXPERIMENT

2.1. Sample characterization

Three model alloys based on Fe-C-Cr were studied. These alloys contained carbon of 0.34 wt% and chromium in the range of 0.92 - 4.76 wt%. Chemical composition that was determined directly on samples for thermal analysis is presented in **Table 1**.

Table 1 Chemical composition of studied alloys /wt%

Alloy	C	Cr	O	Ni	P	S	Mn	Al	W
A	**0.344**	**0.924**	0.002	0.001	0.005	0.068	0.056	0.010	-
B	**0.342**	**2.970**	0.020	0.002	0.004	0.052	0.050	0.008	0.024
C	**0.340**	**4.760**	0.002	0.001	0.002	0.006	0.042	0.004	0.044

The samples for DSC analysis were processed into the form of cylinders with a diameter of 5 mm and a height of 8 mm. The mass of the cylinders was 1 250 ± 10 mg. The samples were polished (the possible oxidation layer was removed) and cleaned by ultrasonic impact in acetone before analysis. Calibration was performed using Pt (3N5) for all alloys.

Structural and phase analysis was performed with the use of the Olympus IX70 optical microscope in a BF light field. These analyses were performed on the alloys in the original state (before thermal analysis).

2.2. Experimental conditions

For obtaining the heat capacities with the help of Differential Scanning Calorimetry (DSC)was used Setaram MHTC (Multi High-Temperature Calorimeter) 96 (with 3D DSC sensor, B-type). The measurements were carried out in alumina crucibles with a volume of 360 µl. An empty corundum crucible served as a reference sample. Dynamic atmosphere of argon was maintained in the furnace during analysis to protect the sample against oxidation. The purity of argon was higher than 99.9999 %.

There were experimentally obtained “apparent heat capacities”- heat capacities including the latent heat of the phase transition. Heat capacities were obtained using the continuous method. Three measurements were carried out under the same experimental conditions. The first measurement was done with the empty corundum crucible (blank), the second measurement was done with the reference sample Pt (3N5), and the last measurement was done with model alloy. The heating rate was 5 °C/min, and the cooling rate was 10 °C/min. Each type of alloy was observed by two measurements at the same conditions at the controlled cycling experiments - two heating runs and two cooling runs.

3. THEORETICAL CALCULATIONS

Theoretical calculations were performed using thermodynamic SW Thermo-Calc, version 2017b and TCFE8.1 database (recommended for Fe-based alloys calculations) and with the CALPHAD method. Elements O, P, S are not included in calculations; diamond and graphite phases are also excluded.

SW Thermo-Calc does not calculate the heat capacity directly but as a function of temperature and enthalpy. It is based on the relation:

$$cp=dH/dT(J/(K\cdot g)) \quad (1)$$

where cp is heat capacity (J/(K·g)), H is enthalpy (J) and T is temperature (K).

4. RESULTS AND DISCUSSION

The heat capacities in the temperature range from 457.15 K to 1852.15 K were studied for all alloys. Experimental values were compared with theoretical values obtained by SW Thermo-Calc**.** Measured experimental values of three experimental measurements and theoretical values are presented in **Figure 1, Figure 3** and **Figure 5**. In the figures, there are marked temperatures of phase transitions at the experimental curves. The start of α →γ is marked as $T_{\alpha\rightarrow\gamma,S}$ and the end is marked as $T_{\alpha\rightarrow\gamma,E}$. The Curie temperature is marked as T_C. The temperature of solidus is market as T_S, the start of peritectic transformation is marked as T_P, and the temperature of liquidus is marked as T_L.

4.1. Alloy A

From the dependence of heat capacities on temperature, it is clear, that experimentally and theoretically obtained values show the same trend within the temperature range, i.e. 457.15 - 1017.15 K, 1104.15 - 1713.15 K and 1804.15 - 1853.15 K, (**Figure 1**). The experimentally obtained heat capacities are within the range of 0.46 - 0.93 J/(K·g) and the calculated ones are in the range of 0.52 -1.03 J/(K·g).

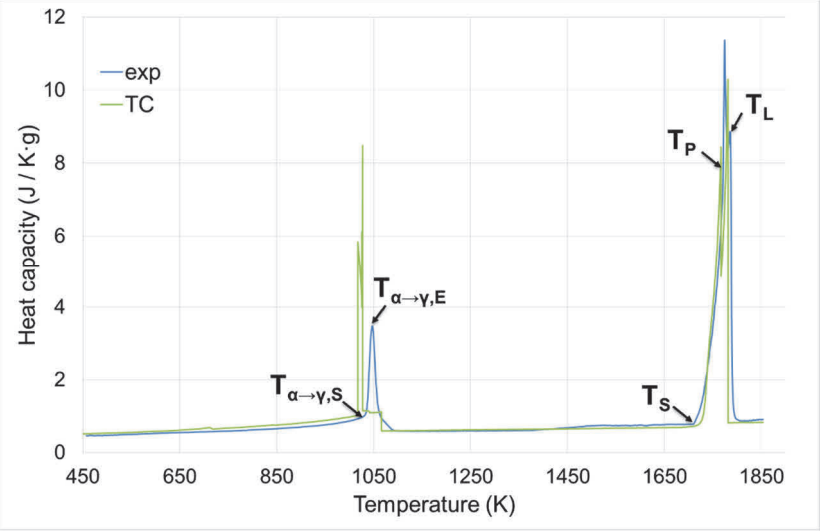

Figure 1 Comparison of experimentally and theoretically heat capacities of alloy A

Figure 2 A perlite-ferritic structure of alloy A

The experimentally determined maximum in the phase transformation of α→γ is 3.48 J/(K·g), and the calculated maximum of this transformation is 8.37 J/(K·g). The difference between the experimental and theoretical maximum is 4.89 J/(K·g). The experimentally determined maximum in the melting range is 11.37 J/(K·g) and the calculated maximum is 10.26 J/(K·g). The difference between the experimental and theoretical maximum is 1.11 J/(K·g). This difference is lower than by transformation of α→γ.

Structural and phase analysis was performed for this alloy (**Figure 2**). Alloy A has a perlitic structure with ferritic girding.

4.2. Alloy B

From the dependence of heat capacities on temperature, it is clear, that experimentally and theoretically obtained values show the same trend within the temperature range, i.e. 457.15 - 1047.15 K, 1100.15 - 1693.15 K and1799.15 - 1853.15 K, (**Figure 3**). The experimentally obtained heat capacities are within the

range of 0.44 - 1.07 J/(K·g), and the calculated ones are in the range of 0.52 - 1.11 J/(K·g). The experimentally determined maximum in the phase transformation of α→γ is 3.29 J/(K·g) and the calculated maximum of this transformation is 5.42 J/(K·g). The difference between the experimental and theoretical maximum is 2.13J/(K·g). The experimentally determined maximum in the melting range is 11.41 J/(K·g), and the calculated maximum is9.84 J/(K·g). The difference between the experimental and theoretical maximum is 1.57 J/(K·g). This difference is lower than by transformation of α→γ.

Structural and phase analysis was performed for this alloy (**Figure 4**). Alloy B has a bainitic structure with the local carbides and perlite residues.

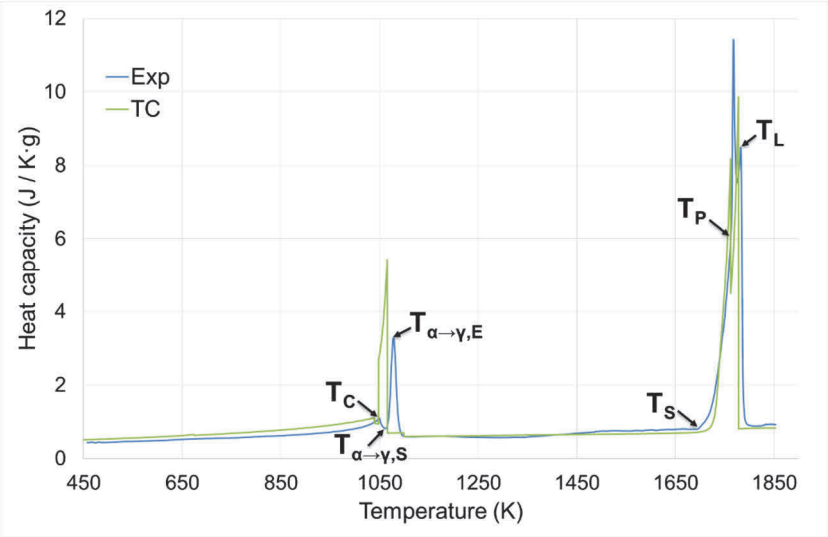

Figure 3 Comparison of experimentally and theoretically heat capacities of alloy B

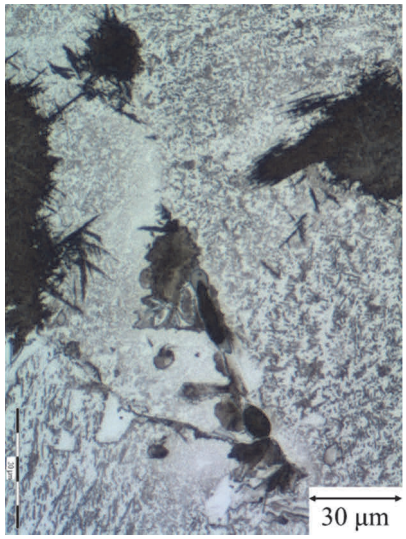

Figure 4 A bainite-perlitic structure of alloy B

4.3. Alloy C

From the dependence of heat capacities on temperature, it is clear, that experimentally and theoretically obtained values show the same trend within the temperature range, i.e. 457.15 - 1070.15 K, 1108.15 - 1713.15 K and 1804.15 - 1853.15 K, (**Figure 5**).

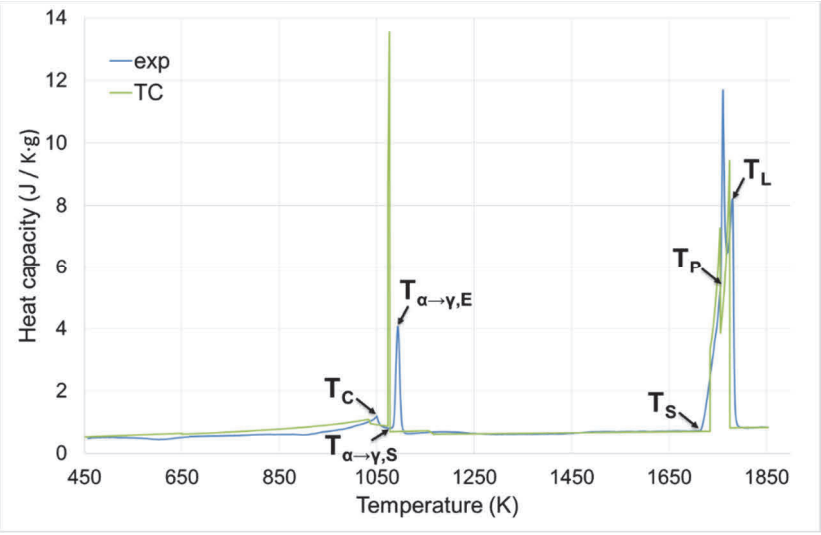

Figure 5 Comparison of experimentally and theoretically heat capacities of alloy C

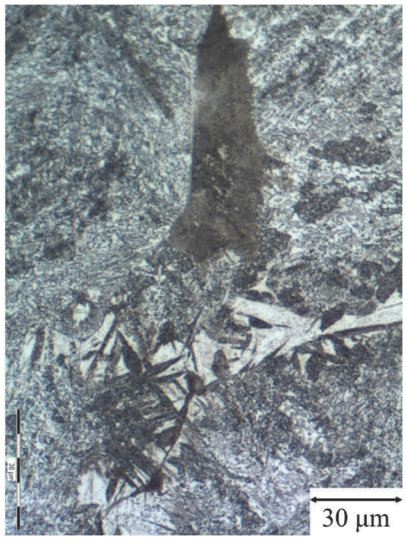

Figure 6 A martensitic-bainite-perlitic structure of alloy C

The experimentally obtained heat capacities are within the range of 0.44 - 1.19 J/(K·g), and the calculated ones are in the range of 0.53 - 1.09 J/(K·g). The experimentally determined maximum in the phase transformation of α→γ is 4.07 J/(K·g), and the calculated maximum of this transformation is 7.89 J/(K·g). The difference between the experimental and theoretical maximum is 3.82 J/(K·g). The experimentally determined maximum in the melting range is 11.68 J/(K·g) and the calculated maximum is 9.42 J/(K·g). The difference between the experimental, and theoretical maximum is 2.26 J/(K·g). This difference is lower than by transformation of α→γ.

Structural and phase analysis for alloy C is in **Figure 6**. This alloy has a martensitic structure with the bainite and sulfides.

5. CONCLUSION

The heat capacities were studied by DSC method. These heat capacities were discussed and compared with the theoretical calculations using SW Thermo-Calc. For all alloys was performed structural and phase analysis. The experimentally obtained heat capacities are relatively close to the calculated values in the high-temperature area. More pronounced differences are between experimental and theoretical values of heat capacities in the low-temperature area. Experimentally obtained heat capacities decrease with increasing content of chromium except for phase transformations in the temperature range of 1371.15 - 1853.15 K. In the high-temperature area, with increasing content of chromium, the maximum heat capacities are being increased, which are also shifted to the lower temperature. There is not an unequivocal trend in increase or decrease of experimental heat capacities with increasing content of chromium in the temperature range of 457.15 - 1370.15 K. In the low-temperature area, there is no clear trend of shifting of the maximum heat capacities, which are shifted to the higher temperatures.

Values of the heat capacities are mostly calculated only concerning the chemical composition, but the heat capacities value (dependence) may be influenced by structure, phases present in the sample and influenceof the deformational state. Therefore, the best way to obtain proper data for the system under investigation is by carrying out an experiment.

The heat capacities of alloys based on Fe-C (steels) are one of the crucial thermophysical parameters used for process behaviour prediction in many applications (thermal treatment of steels) in SWs Magmasoft, Procast.

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