EXPERIMENTAL AND THEORETICAL DETERMINATION OF SPECIFIC HEATS, PHASE TRANSFORMATIONS TEMPERATURES AND ENTHALPY OF FE-C-CR-NI ALLOWS

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Abstract

Knowledge of thermodynamical and thermophysical properties of materials plays an important role for many industrial applications. The paper is dedicated to the study of three model alloys based on Fe-C-Cr-Ni. The studied alloys contained carbon in a range of 0.33 – 0.36 wt%, chromium 1.08 – 4.70 wt% and nickel 1.04 – 4.96 wt%. Thermophysical and thermodynamical properties depending on the composition of alloys such as specific heats, phase transformations temperatures and enthalpy were studied in low and high temperature areas. Experimental data were obtained using following devices: Setaram Sensys Evo and Setaram MHTC Line 96 with 3D DSC sensors. Specific heats were obtained using the continuous method. All measurements were performed in a helium atmosphere. The same properties were calculated using SW Thermo-Calc, then were compared and discussed with experimental data.

Keywords: Fe-C-Cr-Ni alloys, specific heats, phase transformations temperatures, enthalpy, low and high temperature areas

1. INTRODUCTION

Studying of thermodynamical and thermophysical properties of systems based on Fe is very important, because these materials are used almost in all sectors of modern production. These properties are needed for understanding the basis of fundamental behavior of materials depending on their composition and various experimental conditions [5]. Specific heats, phase transformations temperatures, enthalpy, entropy, Gibbs energy and other properties are the main material data for the thermodynamic and thermophysical description of materials [1-2,6]. Many of properties are often studied using thermal analysis methods and calorimetry, which denote a variety of measuring methods.

Performed study presents specific heats, temperatures of transformation of α→γ, solidus and liquidus and enthalpy of laboratory prepared Fe-C-Cr-Ni alloys obtained by Differential Scanning Calorimetry (DSC). These data were discussed and compared with results calculated using one of the most powerful software package for thermodynamic calculations Thermo-Calc.

2. EXPERIMENT

2.1. Sample characterization

The studied alloys contained carbon in a range of 0.33 – 0.36 wt%, chromium 1.08 – 4.70 wt% and nickel 1.04 – 4.96 wt%. The samples for a thermal analysis were in cylindrical forms with following characteristics: diameter was 5 mm and height 8 mm, mass was approximately 1250 mg. The samples were polished and then cleaned in acetone using ultrasound.

The chemical composition of three model alloys based on Fe-C-Cr-Ni is presented in **Table 1**.

Table 1 Chemical composition of alloys (wt%)

Alloy	C	Cr	Ni	Mn	Cu	Co	W
A	0.360	1.080	1.040	0.030	0.012	-	-
B	0.340	2.950	3.040	0.027	0.014	0.013	0.030
C	0.360	4.700	4.960	0.034	0.014	0.015	-

Minor elements content in the studied alloys were in the following intervals: O (up to 0.004 wt%), P (up to 0.004 wt%), S (up to 0.004 wt%), Si (up to 0.003 wt%), Al (up to 0.004 wt%), Ti (up to 0.001 wt%), Mo (up to 0.001 wt%), N (up to 0.005 wt%), B (up to 0.002 wt%).

2.2. DSC – Differential scanning calorimetry and experimental conditions

Experimental data of thermodynamical and thermophysical properties depending on the composition of alloys were obtained using Setaram Sensys Evo and Setaram MHTC Line 96 with a 3D DSC sensor. The measurements were carried out in a low and high temperature areas as well in the atmosphere of helium with purity at least 6 N to protect the samples against oxidation. Temperature calibration was done using Pd and Au for all samples. An empty corundum crucible was as a reference sample. The heating rate was 5 °C/min. Specific heats (apparent heat capacities) were obtained using the continuous method (continuous linear heating or cooling in the controlled atmosphere) [3]. The heat flux of studied samples was measured relative to the heat flux of the reference sample. Enthalpic calibration was performed using Pt (3N5) for all alloys.

3. THEORETICAL BACKGROUND

Theoretical values of specific heats, phase transformations temperatures and enthalpy were calculated by use of thermodynamic SW Thermo-Calc, which has a high-quality database for various materials including Fe-based alloys as well. Elements such as O, P, S, N, B and diamond and graphite phases were not included for calculations. Used SW does not calculate specific heats directly; specific heats were calculated using suitable equation based on the next relation (equation 1) [4]:

$$Cp = dH/dT \quad (J/K \cdot g) \tag{1}$$

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

As for phase transition temperatures, temperatures of transformation of α→γ, solidus and liquidus temperatures were obtained using calculated phase diagrams.

4. RESULTS AND DISCUSSION

4.1. Specific heats

The specific heats of alloys A, B and C were studied in the temperature intervals from 30 ºC to 1580 ºC. Theoretical values of the heat capacities were obtained by SW Thermo-Calc and compared with measured experimental values. Obtained experimental and theoretical values of the specific heats are presented in the **Figures 1 – 3.**

Alloy A

From the dependence of specific heats on temperature (**Figure 1**) can be seen, that obtained experimental and theoretical data have the same trend in the temperature intervals: 30 ºC to 717 ºC, 799 ºC to 1432 ºC and 1522 to 1580 ºC. In these temperature intervals experimental values of specific heats are 0.37 – 1.06 J/K·g

and theoretical values of specific heats are 0.45 – 0.96 J/K·g. In the region of phase transformation α→γ the highest experimental value of the specific heat is 4.88 J/K·g and the highest theoretical value of the specific heat is 6.44 J/K·g, difference between these values is 1.56 J/K·g. In the melting range the highest experimental value of the specific heat is 10.92 J/K·g and the highest theoretical value of the specific heat is 12.42 J/K·g, difference between these values is 1.50 J/K·g.

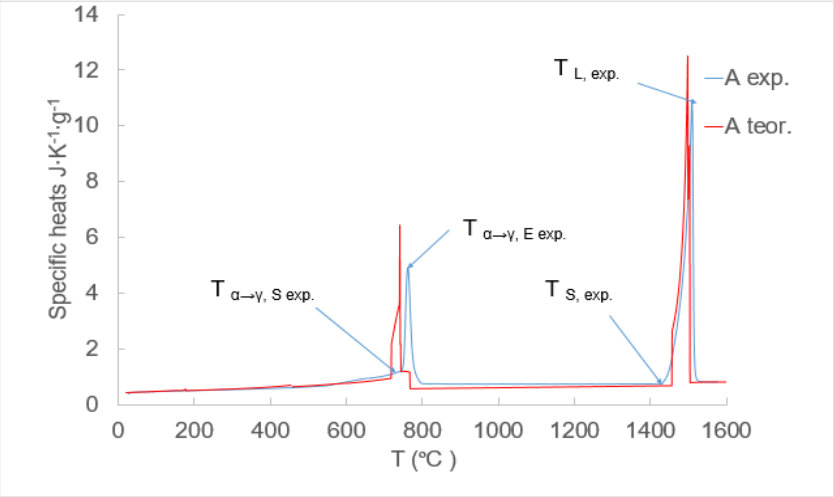

Figure 1 Comparison of experimental and theoretical heat capacities of alloy A

Alloy B

From the dependence of specific heats on temperature (**Figure 2**) it is clear, that obtained experimental and theoretical data have the same trend in the temperature intervals: 30 ºC to 669 ºC, 786 ºC to 1420 ºC and 1517 to 1580 ºC. In these temperature intervals experimental values of specific heats are 0.36 – 0.77 J/K·g and theoretical values of specific heats are 0.45 – 0.91 J K·g. In the range of phase transformation α→γ the highest experimental value of the specific heat is 2.85 J/K·g and the highest theoretical value of the specific heat is 2.73 J/K·g, difference between these values is 0.12 J/K·g. In the melting range the highest experimental value of the specific heat is 11.29 J/K·g and the highest theoretical value of the specific heat is 16.13 J/K·g, difference between these values is 4.84 J/K·g.

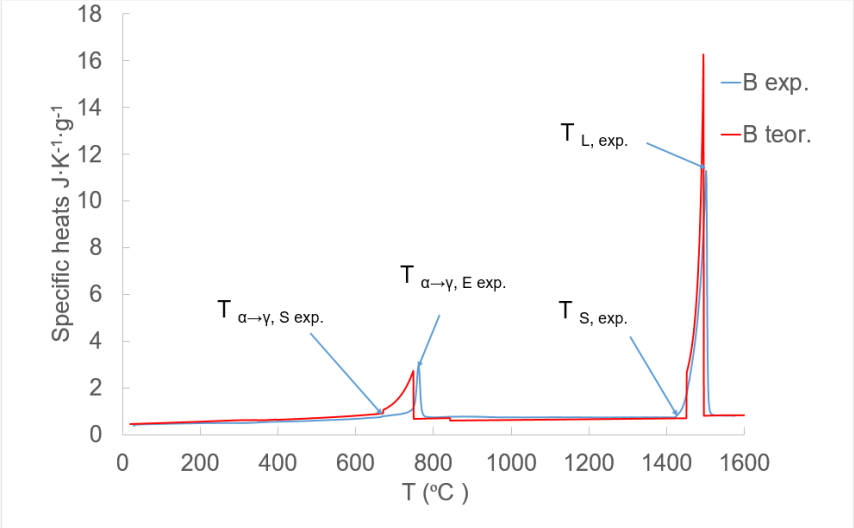

Figure 2 Comparison of experimental and theoretical heat capacities of alloy B

Alloy C

From the dependence of specific heats on temperature (**Figure 3**) it is visible, that obtained experimental and theoretical data have the same trend in the temperature intervals: 30 ºC to 620 ºC, 793 ºC to 1419 ºC and 1509 to 1580 ºC. In these temperature intervals experimental values of specific heats are 0.39 – 0.78 J/ K·g and theoretical values of specific heats are 0.46 – 0.93 J/K·g. In the region of the phase transformation α→γ the highest experimental value of the specific heat is 0.98 J/K·g and the highest theoretical value of the specific heat is 2.11 J/K·g, difference between these values is 1.13 J/K·g. In the melting range the highest experimental value of the specific heat is 10.41 J/K·g and the highest theoretical value of the specific heat is 13.56 J/K·g, difference between these values is 3.15 J/K·g.

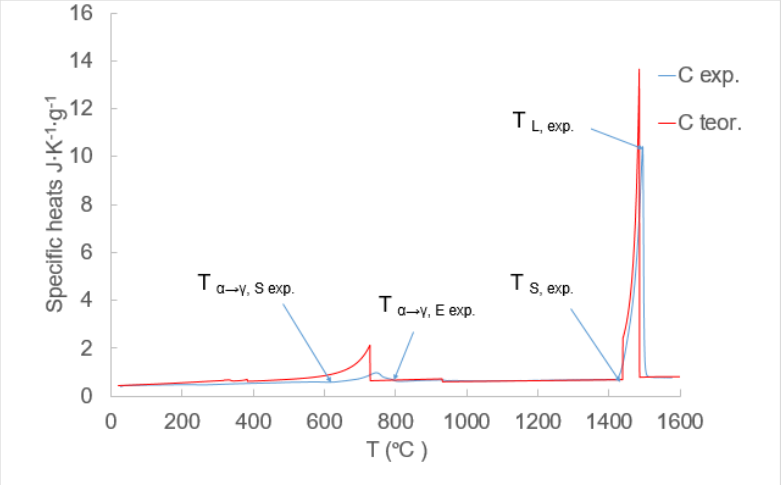

Figure 3 Comparison of experimental and theoretical heat capacities of alloy C

In accordance with received data of dependence of specific heats on temperature and content of studied alloys, we can find out next regularity: the lowest values of specific heats were obtained for alloy with the highest content of nickel and chromium in the phases of liquidus and solidus.

4.2. Phase transformations temperatures

Experimental and theoretical values of phase transformations temperatures of studied alloys are in **Table 2**.

As for phase transformations temperatures, experimental values were detected from DSC curves and are presented and marked in the **Figures 1 – 3** and presented in **Table 2**. Theoretical values of phase transformations temperatures were obtained by SW Thermo-Calc (temperatures are presented and marked in the **Figures 1 – 3** and **Table 2** as well) and compared with experimental values. The start and end of α →γ transformation are marked as $T_{\alpha\rightarrow\gamma,S}$ and $T_{\alpha\rightarrow\gamma,E}$, the temperatures of liquidus and solidus are marked as T_L and T_S. $T_{\alpha\rightarrow\gamma,S}$, $T_{\alpha\rightarrow\gamma,E}$ and T_S show the highest differences between teoretical and experimental values, because it is difficult to determine it by thermal analysis methods.

Table 2 Experimental and theoretical values of phase transformations temperatures of studied alloys

	alloy **A**		alloy **B**		alloy **C**	
Temperature	DSC	TC	DSC	TC	DSC	TC
$T_{\alpha\rightarrow\gamma,S}$	748	717	750	670	620	-
$T_{\alpha\rightarrow\gamma,E}$	791	766	774	748	802	727
T_S	1434	1456	1422	1447	1427	1437
T_L	1498	1502	1492	1493	1485	1485

From **Table 2** it is evident, that with increasing content of nickel and chromium in studied alloys the temperature of liquidus decreases correspondingly, differences between experimental and theoretical values were minimal. As to start and end of α →γ and temperature of solidus, there is no ambiguous trend. Alloy B has the highest $T_{\alpha\rightarrow\gamma,S}$ and alloy C has the lowest $T_{\alpha\rightarrow\gamma,S}$. Alloy C has the highest $T_{\alpha\rightarrow\gamma,E}$ and alloy B has the lowest $T_{\alpha\rightarrow\gamma,E}$. Alloy A has the highest T_S and alloy C has the lowest T_S.

4.3. Dependence of enthalpy on temperature

Experimental values of enthalpy are presented in **Figure 4**. Obtained experimental and theoretical data have the same trend in studied temperature intervals: 30 ºC to 1580 ºC, from **Figure 4** it is clear, that with increasing of temperature enthalpy increases as well. The highest standard deviations are in the range of phase transformations. The highest value of standard deviation for alloy C is 70.83 J/g and for alloy A is 33.81 J/g in the melting range, for alloy B is 60.32 J/g in the range of phase transformations α →γ.

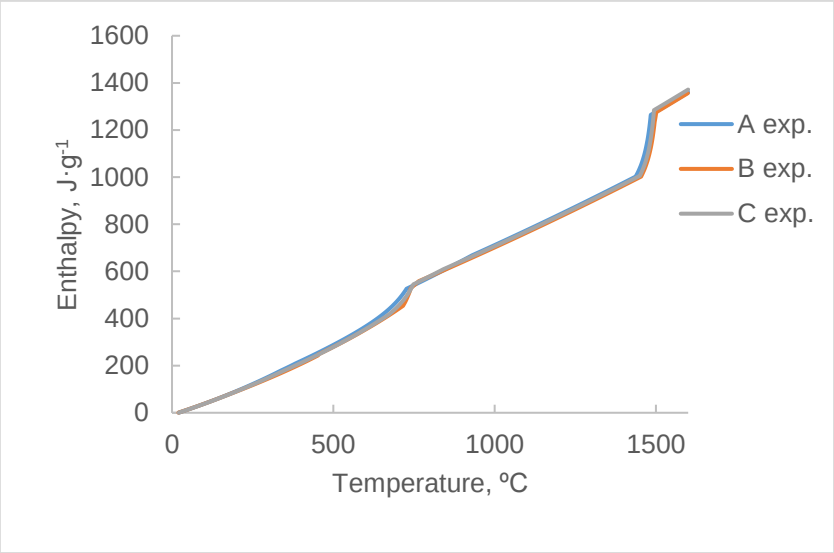

Figure 4 Dependence of experimental values of enthalpy on temperature

5. CONCLUSION

In the presented work specific heats, phase transformations temperatures and enthalpy of three alloys based on iron, nickel, carbon and chromium were studied in low and high temperature areas using DSC and SW Thermo-Calc. The specific heats decrease with increasing content of nickel and chromium in the area outside of phase transformations. The highest differences between theoretical and experimental phase transformations temperatures were in case of $T_{\alpha\rightarrow\gamma,S}$ (diference up to 80 ºC), the best match was obtained for T_L (difference up to 4 ºC). Except specific heats and phase transformations temperatures, dependence of enthalpy on temperature was experimentally determined. New original experimental data were obtained for studies alloys.

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