STUDY OF SPECIFIC HEATS AND PHASE TRANSFORMATION TEMPERATURES OF ALLOYS BASED ON FE-C-CR-NI DEPENDING ON COMPOSITION AND TEMPERATURE

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Abstract

Steels are commonly used metallic materials, that's why higher requirements are imposed on their properties. Thermodynamical and thermophysical properties are one of the most important quantities of materials, which are needed for understanding behavior of materials under defined conditions. Thermal analysis has been widely used in various scientific fields, it can be used for study thermophysical and thermodynamic properties as well. The aim of the paper is study of six model alloys based on Fe-C-Cr-Ni, which contained carbon in a range of 0.0023 – 0.0095 wt%, chromium 0.0050 – 4.5528 wt% and nickel 0.0020 – 4.9600 wt%. Specific heats and phase transformations temperatures were studied in a high-temperature area. Experimental data were obtained using Setaram MHTC 96 Line with a 3D DSC sensor. Theoretical data were calculated using SW Thermo-Calc and JMatPro, then were compared and discussed with experimental data.

Keywords: Fe-C-Cr-Ni alloys, specific heats, phase transformations temperatures, high temperature area

1. INTRODUCTION

Thermal analysis is a group of techniques in which a property of the sample is monitored against time or temperature while the temperature of the sample, in a specified atmosphere, is programmed. Differential scanning calorimetry (DSC) is a thermoanalytical technique in which the difference in the amount of heat required to increase the temperature of a sample and reference is measured as a function of temperature. The method DSC was used for achieving the aim – of obtaining experimental data of specific heats and phase transformation temperatures, such as temperatures of transformation of α→γ, γ→δ, solidus, liquidus and Curie temperatures of laboratory prepared Fe-C-Cr-Ni alloys. These data were discussed and compared with theoretical results calculated using SW Thermo-Calc and JMatPro.

Thermal analysis is used for study of thermophysical and thermodynamic properties of quaternary systems based on iron, carbon, chromium, and nickel [1-2]. It is important to know thermodynamic and thermophysical properties of these materials (the properties of materials are changed in the field of phase transformations) because they are used almost in all branches of modern production. These properties are the main material data for description of the behavior depending on the chemical and phase composition and experimental conditions (temperature) [3,4].

There is still not enough accurate experimental data, that could be used for creation and clarification of databases based on Fe-C-Cr-Ni and for simulation of metallurgical processes. That is why the study of systems based on Fe-C-Cr-Ni has received substantial interest.

2. EXPERIMENT

2.1. Sample characterization

The studied alloys contained major elements, such as carbon in a range of 0.0023 – 0.0095 wt%, chromium 0.0050 – 4.5528 wt% and nickel 0.0020 – 4.9600 wt%. The samples had the form of a cylinders, diameter of samples was 5 mm and height of samples was 8 mm, mass of every sample was approximately the same 1,250 ± 10 mg. They were polished and cleaned in acetone using ultrasound. The studied samples were made by induction melting using furnace Leybold Heraus in the laboratory and then were analyzed using thermal analysis. The chemical composition of six model alloys based on Fe-C-Cr-Ni is presented in **Table 1**.

Table 1 Chemical composition of the major elements of studied alloys /wt%

Alloy	C	Cr	Ni	Mn	Cu	O
A	0.0030	0.0090	4.8300	0.0160	0.0150	0.0560
B	0.0030	0.0050	4.9600	0.0120	0.0150	0.0900
C	0.0023	4.5528	0.0025	0.0340	0.0070	0.0317
D	0.0032	4.3860	0.0020	0.0240	0.0060	0.0367
E	0.0095	4.0300	4.7850	0.0230	0.0130	0.0715
F	0.0062	4.3940	4.4930	0.0140	0.0130	0.0642

2.2. DSC – Differential scanning calorimetry

Experimental data of specific heats and phase transformation temperatures were gotten by DSC method for a studied alloys A, B, C, D, E, F using Setaram MHTC 96 Line with a 3D DSC sensor, in a high-temperature area and in the atmosphere of helium with purity at least 6 N for a protection of the samples against oxidation. The heating rate was 5°C/min. The corundum sleeve was placed in a Pt crucible and covered with corundum vices and Pt vices, both in the sample and reference cells. Continuous method, which consists of three measurements: the first is called "blank" with an empty measuring and comparison crucible, the second measurement is performed with a standard (Pt) of known mass and known heat capacity and the third measurement is performed using sample of known mass, which is placed in a measuring crucible and the reference crucible is again empty, was used for determining specific heats. To obtain precise values of specific heats, it is necessary to perform temperature and enthalpic calibration. Temperature calibration was done using Pd, Ag, Au.

3. THEORETICAL BACKGROUND

Theoretical values of specific heats and phase transformations temperatures were calculated by use of thermodynamic SW Thermo-Calc, which has database for various materials, including Fe-based alloys, and SW JMatPro, which calculates a wide range of materials properties for alloys. The results were obtained by SW Thermo-Calc version 2019a using the TCFE8 database and SW JMatPro version 11.1 using General Steel database. Elements such as O, P, S, N, B, and diamond and graphite phases were not included for calculations in SW Therno-Calc and N was not included for calculations in SW JMatPro. The specific heats were calculated in SW Thermo-Calc using next equation (1) [5], while SW JMatPro calculate the specific heats directly.

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

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

4. RESULTS AND DISCUSSION

4.1. Comparison of experimentally and theoretically specific heats of alloys

The specific heats of alloys A, B, C, D, E, F were studied in the temperature intervals from 500 ºC to 1,580 ºC. Theoretical values of the heat capacities were gotten by SW Thermo-Calc and JMatPro and compared with measured experimental values. In this section selected obtained experimental and theoretical values of the specific heats (of alloy D with high content of chromium) are illustrated in the **Figure 1**.

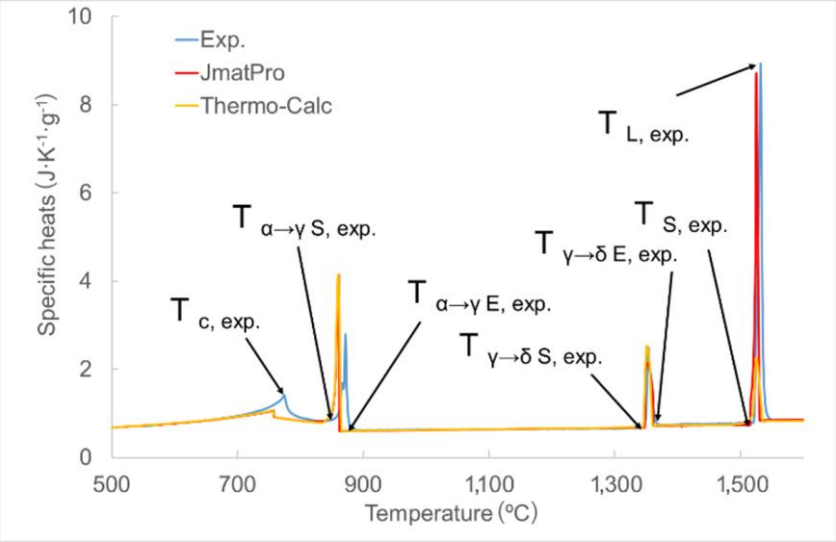

Figure 1 Experimental and theoretical heat capacities of alloy D

From the dependence of specific heats on temperature (**Figure 1**) we can see, that obtained experimental and theoretical data have the same trend in the next temperature intervals: 500 - 728 ºC, 885 – 1,344 ºC, 1,373 - 1,511 ºC and 1,551 – 1,580 ºC. In these temperature intervals experimental values of specific heats are 0.62 – 1.04 J/ K·g, theoretical values of specific heats (obtained by SW Thermo-Calc) are 0.60 – 0.99 J/ K·g and theoretical values of specific heats (obtained by SW JMatPro) are 0.60 – 0.99 J/ K·g. The results demonstrate, that the highest and the lowest deviations of experimental data from theoretical values (in case of SW Thermo-Calc) are 0.13018 J/ K·g and 0.00012 J/ K·g, 0.10002 J/ K·g and 0.00026 J/ K·g – in case of SW JMatPro.

In the α→γ phase transformation the highest experimental value of the specific heat is 2.79 J/ K·g and the highest theoretical value of the specific heat is 4.13 J/ K·g (obtained by SW Thermo-Calc and SW JMatPro), difference between these values is 1.34 J/ K·g. In the γ→δ phase transformation the highest experimental value of the specific heat is 2.49 J/ K·g, the highest theoretical value of the specific heat is 2.49 J/ K·g (obtained by SW Thermo-Calc) and 2.13 J/ K·g (obtained by SW JMatPro), difference between experimental and theoretical values (obtained by SW JMatPro) is 0.36 J/ K·g. In the malting range the highest experimental value of the specific heat is 8.93 J/ K·g, the highest theoretical value of the specific heat is 2.26 J/ K·g (obtained by SW Thermo-Calc) and 8.58 J/ K·g (obtained by SW JMatPro), differences between experimental and theoretical values are 6.67 J/ K·g and 0.35 J/ K·g respectively.

As for alloys A, B, C, E and F, obtained experimental values of the specific heats also were compared with calculated theoretical data in SW Thermo-Calc and JMatPro.

4.2. Dependence of specific heats on the content of studied alloys

The specific heats of alloys in the temperature range 550 – 1,580 ºC were obtained using Setaram MHTC 96 Line with a 3D DSC sensor. Experimental values of the specific heats are in the **Figure 2 – Figure 5**.

From the **Figure 2** we can see, that experimental values of specific heat are 0.67 – 0.99 J/ K·g in the temperature range 550 - 730 ºC, alloy C has the highest values of specific heat and alloy E has the lowest values of specific heat. The specific heats of studied alloys increase, when the content of chromium increases, the specific heats decrease, when the content of nickel increases. As for alloys E and F, which have the high content of chromium and nickel, alloys have the similar trend of specific heats, alloy F has higher values of specific heats.

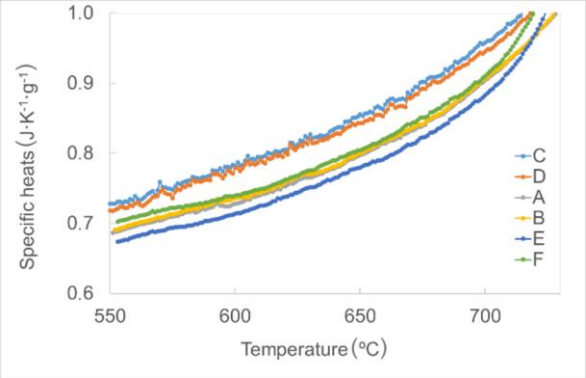

Figure 2 Experimental values of specific heats of alloys A, B, C, D, E and F in the temperature range 550 - 730 ºC

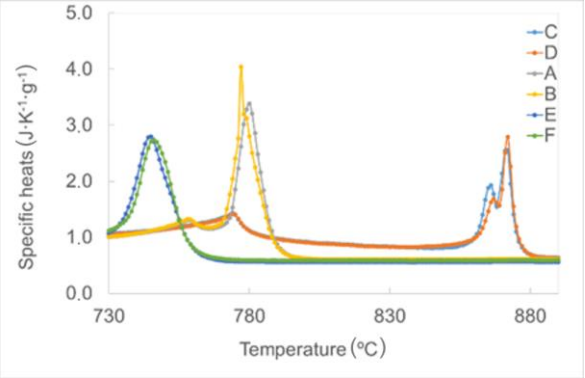

Figure 3 Experimental values of specific heats of alloys A, B, C, D, E and F in the temperature range 730 - 890 ºC

From the **Figure 3** we can find out, that experimental values of specific heat are 0.59 – 1.08 J/ K·g in the temperature range 730 - 890 ºC (except the temperature range of α→γ phase transformation), alloy C has the highest values of specific heat and alloy E has the lowest values of specific heat. The specific heats of studied alloys increase, when the contents of chromium and nickel increase. As for alloys E and F, which have the high content of chromium and nickel, alloys have the similar trend of specific heats, alloy F has higher values of specific heats.

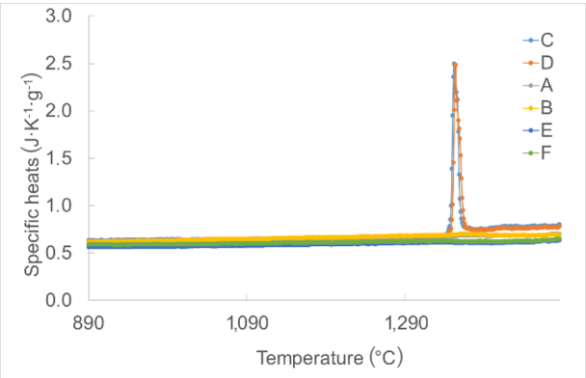

Figure 4 Experimental values of specific heats of alloys A, B, C, D, E and F in the temperature range 890 – 1,485 ºC

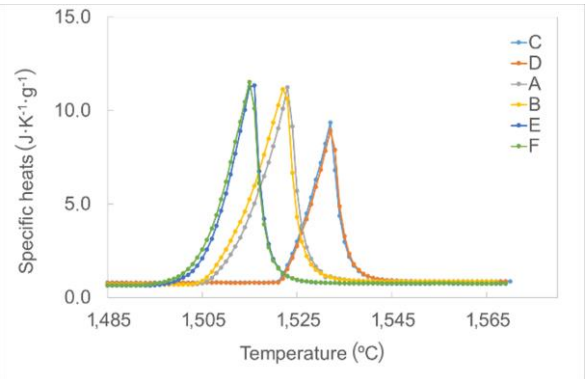

Figure 5 Experimental values of specific heats of alloys A, B, C, D, E and F in the temperature range 1,485 – 1,580 ºC

From the **Figure 4** we can see, that experimental values of specific heat are 0.56 – 0.80 J/ K·g in the temperature range 890 – 1,485 ºC (except the temperature range of γ→δ phase transformation), alloys A, B, C, D have the highest identical values of specific heat and alloy E has the lowest values of specific heat. The specific heats of studied alloys increase, when the contents of chromium and nickel increase. As for alloys E

and F, which have the high content of chromium and nickel, alloys have the similar trend of specific heats, alloy F has higher values of specific heats.

From the **Figure 5** we can find out, that experimental values of specific heat are 0.64 – 0.86 J/ K·g in the temperature range 1,485 – 1,580 ºC (except the malting range), alloy C has the highest values of specific heat and alloy E has the lowest values of specific heat. The specific heats of studied alloys increase, when the contents of chromium and nickel increase. As for alloys E and F, which have the high content of chromium and nickel, alloys have the similar trend of specific heats, alloy F has higher values of specific heats.

In accordance with received data of dependence specific heats on temperature and content of studied alloys, we can find out next regularities: the specific heats increase, when the contents of chromium and nickel increase in all temperature interval, except the temperature range 550 - 730 ºC (specific heats of studied alloys increase, when the content of chromium increases, the specific heats decrease, when the content of nickel increases).

4.3. Phase transformations temperatures depending on the content of studied alloys

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

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

T °C	DSC	JMatPro	TC	T °C	DSC	JMatPro	TC
	A				B		
$T_{\alpha\rightarrow\gamma,S}$	773	-	-	$T_{\alpha\rightarrow\gamma,S}$	772	-	-
$T_{\alpha\rightarrow\gamma,E}$	795	760	766	$T_{\alpha\rightarrow\gamma,E}$	794	757	763
$T_{\gamma\rightarrow\delta,S}$	-	-	-	$T_{\gamma\rightarrow\delta,S}$	-	-	-
$T_{\gamma\rightarrow\delta,E}$	-	-	-	$T_{\gamma\rightarrow\delta,E}$	-	-	-
T_S	1,507	1,501	1,516	T_S	1,505	1,501	1,516
T_L	1,517	1,517	1,518	T_L	1,516	1,514	1,518
T_C	759	-	-	T_C	759	-	-
	C				D		
$T_{\alpha\rightarrow\gamma,S}$	865	-	-	$T_{\alpha\rightarrow\gamma,S}$	866	-	-
$T_{\alpha\rightarrow\gamma,E}$	881	861	860	$T_{\alpha\rightarrow\gamma,E}$	881	862	861
$T_{\gamma\rightarrow\delta,S}$	1,343	1,344	1,346	$T_{\gamma\rightarrow\delta,S}$	1,344	1,347	1,350
$T_{\gamma\rightarrow\delta,E}$	1,356	1,356	1,355	$T_{\gamma\rightarrow\delta,E}$	1,350	1,360	1,360
T_S	1,521	1,516	1,529	T_S	1,521	1,515	1,529
T_L	1,527	1,529	1,531	T_L	1,527	1,529	1,531
T_C	774	755	755	T_C	774	755	755
	E				F		
$T_{\alpha\rightarrow\gamma,S}$	736	-	-	$T_{\alpha\rightarrow\gamma,S}$	732	-	-
$T_{\alpha\rightarrow\gamma,E}$	765	733	736	$T_{\alpha\rightarrow\gamma,E}$	766	736	740
$T_{\gamma\rightarrow\delta,S}$	-	-	-	$T_{\gamma\rightarrow\delta,S}$	-	-	-
$T_{\gamma\rightarrow\delta,E}$	-	-	-	$T_{\gamma\rightarrow\delta,E}$	-	-	-
T_S	1,504	1,496	1,492	T_S	1,496	1,492	1,505
T_L	1,509	1,511	1,511	T_L	1,510	1,511	1,512
T_C	-	-	-	T_C	-	-	-

Experimental values were detected from DSC curves and theoretical values were obtained by SW Thermo-Calc and SW JmatPro 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 start and end of γ→δ transformation are marked as $T_{\gamma\rightarrow\delta,S}$ and $T_{\gamma\rightarrow\delta,E}$, the temperature of liquidus and solidus are marked as T_L and T_S, the Curie temperature is marked as T_c.

From **Table 2** we can find out, that alloy F has the lowest experimental $T_{\alpha\rightarrow\gamma,S}$ and alloy D has the highest $T_{\alpha\rightarrow\gamma,S}$, it is impossible to determine theoretical values of $T_{\alpha\rightarrow\gamma,S}$ by SW Thermo-Calc and SW JmatPro. As for $T_{\alpha\rightarrow\gamma,E}$, alloy E has the lowest value and alloy D has the highest value. Some values of T_c are presented in **Table 2**. Sometimes it is impossible to define the Curie temperatures, because it is hidden in α →γ transformation. As for γ→δ phase transformation, it was just in alloys C and D, which have the highest contents of chromium. Alloy C has the lowest values of $T_{\gamma\rightarrow\delta,S}$, as for $T_{\gamma\rightarrow\delta,E}$, there is no ambiguous trend. Alloy F has the lowest T_S and alloys C and D have the highest T_S. Alloy E has the lowest T_L and alloys C and D have the highest T_L.

Analyzing the **Table 2**, we can see, T_L has the lowest deviation of experimental values of from theoretical values (0 – 0.3 %), $T_{\alpha\rightarrow\gamma,E}$ has the highest deviation (2.2 – 4.7 %). In accordance with received data of phase transformations temperatures depending on the content of studied alloys, we can find out next regularities: with increase of content of nickel $T_{\alpha\rightarrow\gamma,S}$, $T_{\alpha\rightarrow\gamma,E}$, T_S, and T_L decrease, with increase of content of chromium $T_{\alpha\rightarrow\gamma,S}$ increases and $T_{\gamma\rightarrow\delta,S}$ decreases. As for other phase transformation temperatures, there are no obvious trends.

5. CONCLUSION

In the presented paper specific heats and phase transformations temperatures of six alloys based on iron, nickel, carbon and chromium were studied in high-temperature area. Experimental values were gotten by DSC method using Setaram MHTC 96 Line with a 3D DSC sensor and compared with theoretical values calculated by use SW Thermo-Calc and SW JmatPro. New original experimental data were obtained for studies alloys.

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