EXPERIMENTAL AND THEORETICAL RESEARCH OF SOLIDUS AND LIQUIDUS TEMPERATURE OF Fe-C-Cr-Ni BASED SYSTEMS

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Abstract

Three model alloys based on Fe-C-Cr-Ni were studied. Alloys contained 0.34 - 0.36 wt. % of carbon and chromium and nickel in the range of 1.04 – 4.96 wt. %. Temperatures of solidus and liquidus were studied. The experimental data were obtained using differential thermal analysis (DTA), differential scanning calorimetry (DSC) and dilatometry. The Setaram Setsys 18TM, Setaram MHTC 96 Line and NETZSCH DIL 402 Expedis Supreme were used for experiments. The experimental data were compared and discussed with the calculation results using SWs IDS, JMaPro and Thermo-Calc and with empirical calculation.

Keywords: Fe-C-Cr-Ni alloys, thermal analysis, solidus temperature, liquidus temperature, IDS, JMatPro, Thermo-Calc

1. INTRODUCTION

Thermophysical and thermodynamic properties of Fe-based systems have been a subject of extensive research. Significant improvement in the quality and efficiency of steel production, reduction of energy consumption, and environmental impact are not possible without accurate estimation of liquidus and solidus temperatures [1]. The temperature of liquidus is technologically significant for the correct setting of casting and solidification conditions. Steel must be overheated to some extent for safe and proper operations regarding the continuous or ingot casting process. If no proper liquidus temperatures exist (is applied) for process adjusting, frequently excessive overheating is applied, leading to energy and time losses and, hence, financial losses and unnecessary environmental burden [2].

The temperature of liquidus and the temperature of solidus are also ones of the input variables for modelling steel production processes in terms of use in control systems and numerical simulations, which supports the development and improvement of recent technology [3]. There is a lack of data for the temperature of solidus in the literature, and those published by various authors for different steel grades alternate in the order of tens of degrees Celsius.

Presently, the determination of liquidus temperatures employing thermal analysis methods usually provides nearly accurate information documented by many authors [2-6]. Knowledge of accurate solidus and liquidus temperatures is essential for the improvement of final steel quality and reduction of production costs.

2. EXPERIMENT

2.1. Sample characterization

Three model alloys based on Fe-C-Cr-Ni were studied. These alloys contained carbon of 0.34 – 0.36 wt% and chromium and nickel in the range of 1.04 – 4.96 wt%. The 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	Ni	O	P	S	Mn	Al	Cu
CrNi1	**0.360**	**1.040**	**1.080**	0.002	-	0.003	0.030	0.004	0.012
CrNi3	**0.340**	**3.040**	**2.950**	0.002	0.004	0.003	0.027	0.004	0.014
CrNi5	**0.360**	**4.960**	**4.700**	0.004	0.004	0.004	0.034	0.002	0.014

The samples for DTA analysis were processed into the form of cylinders with a diameter of 3.5 mm and a high of 3 mm. The mass of the cylinders was 190 mg. Temperature calibration was performed using Pd.

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. Calibration was performed using Pt.

The samples for dilatometric analysis were processed into the form of cylinders with a diameter of 6.35 mm and a length of 10.05 mm. The mass of the cylinders was approximately 2 400 mg. The samples were prepared to fill as much space of the ampoule as possible in which they were analysed. Temperature calibration was performed using Pd.

2.2. Experimental conditions

For obtaining the temperatures of phase transformations with the help of **Differential Thermal Analysis (DTA)** was used **Setaram Setsys 18$_{TM}$**. The measurements were carried out in alumina crucibles with a volume of 80 µl. The 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 %. The samples were analysed with a heating rate of 10 °C/min.

For obtaining the temperatures of phase transformations with the help of **Differential Scanning Calorimetry (DSC)** was used **Setaram MHTC** (Multi High-Temperature Calorimeter) **96 Line** (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. The dynamic atmosphere of helium was maintained in the furnace during analysis to protect the sample against oxidation. The heating rate was 5°C/min.

For obtaining the experimental **dilatometric results** was used **NETZSCH DIL 402 Expedis Supreme** with an S-type thermocouple. The measurements were carried out in sapphire ampoules. The dynamic atmosphere of helium was maintained in the furnace during the analysis. The purity of helium was 99.9999 %. Two measurements were carried out under the same experimental conditions. The heating rate used was 10 °C/min.

3. THEORETICAL CALCULATIONS

Theoretical calculations were performed using thermodynamic SWs IDS (ver. 1.3.1), JMatPro (ver. 11.1 and database of General steel) and Thermo-Calc (ver. 2019a and database of TCFE8.1). Elements O, P, S have not been included in Thermo-Calc (marked as TC) calculations. The calculations were unstable with these elements.

4. RESULTS AND DISCUSSION

The temperatures of phase transformations were studied in the high-temperature area. Temperatures of solidus (T_S) and liquidus (T_L) were detected by DTA, DSC method and dilatometry (DIL). Experimental values were compared with theoretical calculations obtained by SW IDS, JMatPro and Thermo-Calc and with theoretical relations mentioned in [7-10]. **Figure 1** shows the DTA curves obtained for the analysed alloys. Experimental phase transformation temperatures and theoretical values are presented in **Table 2.**

Figure 1 shows that with increasing chromium and nickel content for the solidus temperature, no clear trend of decrease or increase was evident; the temperature of the liquid decreases and the temperature interval in which the melting takes place narrows with increasing chromium and nickel content.

Table 2 Phase transformation temperatures of analyzed alloys CrNi1, CrNi3 and CrNi5

	Experiment			*Calculation*		
°C	***DTA***	***DSC***	***DIL***	***IDS***	***TC***	***JMatPro***
			CrNi1			
T_S	1426	1434	1424	1425	1456	1453
T_L	1494	1498	1510	1502	1502	1503
			CrNi3			
T_S	1423	1422	1422	1411	1451	1448
T_L	1487	1492	1504	1493	1494	1496
			CrNi5			
T_S	1421	1427	1426	1404	1437	1432
T_L	1477	1485	1493	1483	1485	1488

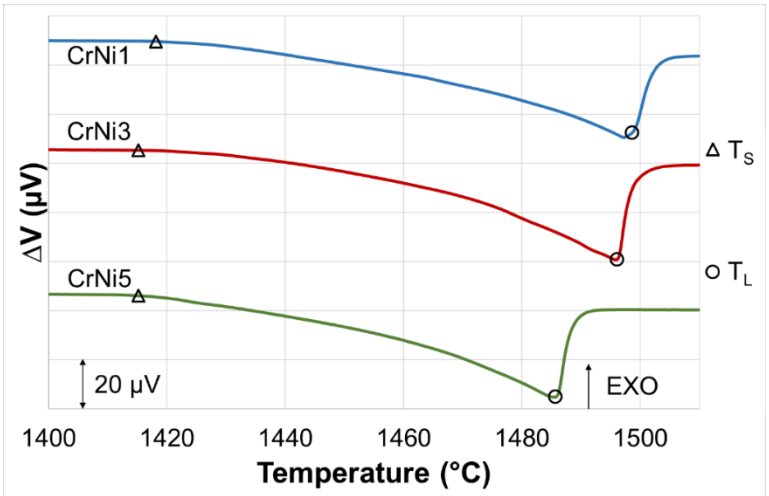

Figure 1 DTA curves of analyzed alloys CrNi1, CrNi3 and CrNi5

The differences between the experimental and theoretically obtained values are from 1 °C for CrNi1 alloys (T_L, DSC-JMatPro; T_S, DIL-IDS; T_S, DTA-IDS) and CrNi3 (T_L, DSC-JMatPro) to 32 °C for the CrNi1 sample (T_S, DIL-TC), **Table 2**. The most significant differences between the experimental and theoretical values were demonstrated for the solidus temperature. The standard deviation between the individual experimental methods was between 0 °C for the CrNi3 sample (T_S, DSC-DIL) and 7 °C for the CrNi1, CrNi3 and CrNi5 samples (T_L, DTA-DIL). In comparing individual software, the best match is between experimental and theoretical values of SW IDS. The differences between the experimental and theoretical values may be due to the fact that the calculations are performed in equilibrium while the experiment is only approaching it. Another reason may be the lack of accurate experimental data for calculations and incomplete databases.

For comparison results of experimental methods with each other and with theoretical calculations with SWs was performed the statistical analysis, **Figures 2 – 5**. It was determined mean squared error (MSE) in °C. The statistical analysis of obtained results shows that the differences in the phase transformations' temperatures compared with the particular experimental methods are from 4 to 12 °C. The best agreement was for

comparing DTA and DSC methods. The differences may be due to the effects of experimental conditions of individual methods, mutual interactions of individual elements and kinetics of phase transformations.

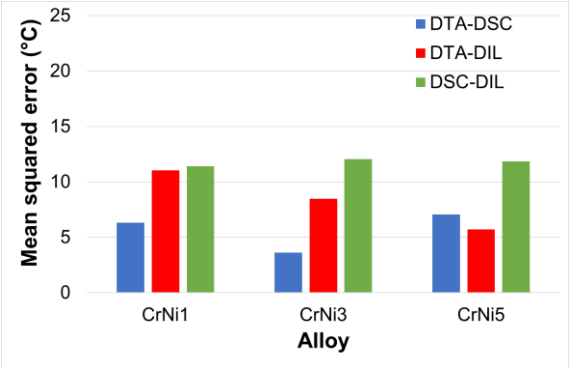

Figure 2 Mean squared error for comparison of results of experimental methods

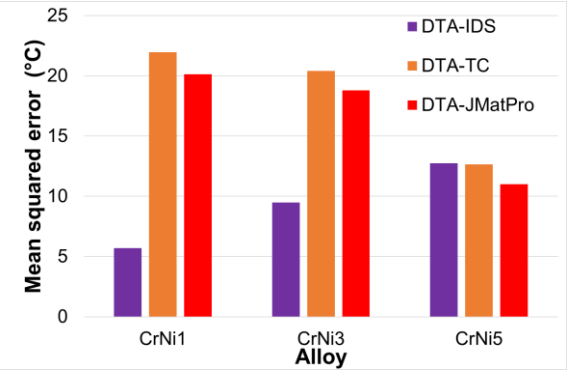

Figure 3 Mean squared error for comparison of results of DTA method and theoretical calculation

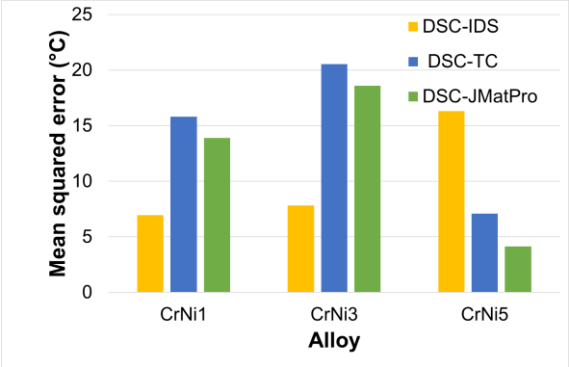

Figure 4 Mean squared error for comparison of results of DSC method and theoretical calculation

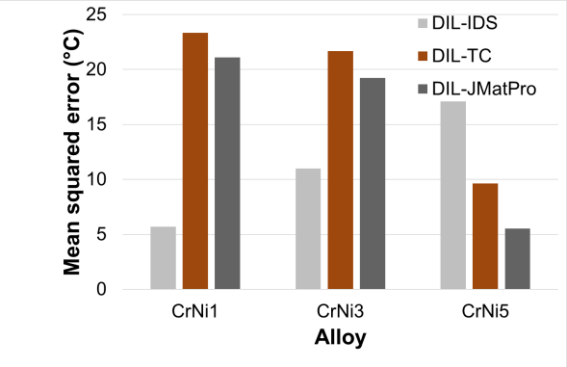

Figure 5 Mean squared error for comparison of results of dilatometry and theoretical calculation

Comparing the experimental results with the theoretical ones determined by calculations in SWs, statistical analysis showed that the best agreement was for CrNi5 alloy (DSC-JMP, MSE = 4° C) and the largest deviation for CrNi1 alloy (DIL-TC, MSE = 23 °C). A better agreement was found for SW IDS and JMaTPro. On the contrary, the biggest differences in comparing all experimental methods with calculations were found for SW Thermo Calc.

Table 3 Calculated values of T_S and T_L according to the available literature

Alloy	T_S			T_L		
	[7]	[8]	[9]	[7]	[8]	[10]
CrNi1	1456	1380	1405	1499	1498	1508
CrNi3	1449	1377	1401	1490	1491	1509
CrNi5	1434	1358	1384	1479	1481	1507

The experimentally obtained phase transformation temperatures were also compared with calculations reported in the available literature. The solidus temperature was calculated according to the equations given in [7-9] and the liquidus temperature according to the equations given in [7,8,10]. The results are shown in **Table 3**.

The differences between experimental and theoretical data are for the temperature of solidus from 7 (CrNi5, DSC [7]) to 69 °C (CrNi5, DSC [8]). Lower differences were found for liquidus temperature. The best match was for alloy CrNi3 (DSC [8], difference 1 °C), and the largest deviation was for CrNi5 alloy (DTA [10], difference 30 °C).

5. CONCLUSION

The experimental results obtained using three thermal analysis methods were compared with calculations using SWs and using theoretical relationships reported in the available literature. The obtained results show that when comparing the temperature of solid and liquid, a better agreement was found for T_L compared to all calculations. In contrast, significant differences up to 69 °C were noted for T_S. This may be due to the fact that the solidus temperature is difficult to determine experimentally, the method of calculation (equilibrium/nonequilibrium) has an effect on its shift, this temperature is less experimental and theoretically examined compared to the liquid temperature, so there are insufficient data for its calculation.

Compared with theoretical calculations obtained with SWs and theoretical relations from the literature, better agreement with experimental results from calculations with SWs was demonstrated. This may be due to the fact that thermodynamic software in the calculation considers the mutual interactions of the individual elements. At the same time, the theoretical equations are based on experimental measurements, where these interactions did not have to be taken into account.

Based on the obtained data, it can be stated that there are still differences (even tens of °C) between experimental and theoretical values**,** and it is**,** therefore**,** necessary to continue the systematic study of phase transformation temperatures of Fe-based systems.

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