THERMAL ANALYSIS AND THEORETICAL CALCULATIONS OF THERMOPHYSICAL PROPERTIES OF Fe-C-Ni BASED ALLOYS

[1]Ľubomíra DROZDOVÁ, [1]Bedřich SMETANA, [1]Mario MACHŮ, [1]Simona ZLÁ, [1]Monika KAWULOKOVÁ, [1]Vlastimil NOVÁK, [1]Lenka ŘEHÁČKOVÁ, [1]Svetlana SOROKINA, [1]Dalibor NOVÁK

[1]VSB - Technical University of Ostrava, Ostrava, Czech Republic, EU, lubomira.drozdova@vsb.cz

https://doi.org/10.37904/metal.2022.4384

Abstract

Three model alloys based on Fe-C-Ni were studied. The alloys containing carbon between 0.338 and 0.382 wt% and nickel between 1.084 and 4.478 wt%. Phase transition temperatures, coefficient of thermal expansion, and density were experimentally and theoretically determined and clarified for all specific alloys in the high-temperature area from 1000 °C to 1595 °C. Phase transition temperatures were experimentally obtained using differential thermal analysis (DTA), differential scanning calorimetry (DSC), and dilatometry. The coefficient of thermal expansion and density were determined by dilatometry. Additionally, experimental data were compared and discussed with calculation results using SW JMatPro, and Thermo-Calc. The obtained experimental results show that with increasing nickel content, the temperature of the liquidus and the coefficient of thermal expansion decrease. Conversely, the density increases with increasing nickel content. The ambiguous influence of nickel on the change in solidus temperature was observed.

Keywords: Fe-C-Ni alloys, thermal analysis, phase transition temperatures, coefficient of thermal expansion, density

1. INTRODUCTION

Iron-based alloys are of great practical importance because they have technical properties that allow their wide use in the construction, energy and machinery industries, the vehicle industry, the consumer industry, medicine – basically everywhere [1,2]. Broad variability of the chemical composition of ferrous alloys, e.g. steels, which represents an example of multiple component alloy, causes a lack of experimental thermophysical and thermodynamical data for each particular alloy [3,4]. Accurate data is needed for proper use in a specific application and in the process of producing semi-finished and finished products from a particular grade of steel as final properties depends not only on the chemical composition but also on the processes of casting, forming, heat or surface treatment, machining, welding etc. [5]. Same data is needed for simulation of manufacturing processes as simulations represents cheaper alternative to physical experiment on actual manufacturing device (blast furnace operation, secondary steel treatment, continuous casting machines, rolling mills or forging machines). Obtained results highly depend on quality of input data so proper experimental data regarding solidus and liquidus and other phase change temperatures, coefficient of thermal expansion and density is required [6].

This paper focuses on the study of phase transition temperatures, coefficient of thermal expansion, and density in the high-temperature area. Three model alloys based on Fe-C-Ni were studied. Experimental results were obtained using differential thermal analysis (DTA), differential scanning calorimetry (DSC), and dilatometry. Experimentally acquired results were discussed with results calculated using SW JMatPro, and Thermo Calc. This work deals with the influence of nickel content to change experimentally and theoretically obtained results.

2. THEORETICAL CALCULATIONS

SW JMatPro (JMP) is a simulation software calculating a wide range of material properties of alloys, focusing mainly on multicomponent alloys used in industrial practice [7]. The results presented in this work were obtained by SW JMatPro version 11.1 and database General Steel. In the calculations for this work, the whole composition of the studied alloys was taken into account.

SW Thermo-Calc (TC) has been developed as a complex heterogeneous system with highly non-ideal as well as ideal solution phases that can be applied to thermodynamic systems in the fields of chemistry, metallurgy, materials science, semiconductors, etc. depending on the type of database used [8]. The software contains several databases, while the TCFE database is mainly used for iron alloys. The work reproduces the results obtained by SW Thermo-Calc version 2019a using the TCFE8 database. Elements H, P, S were not included in the calculations. The representation of these elements in the calculation caused its instability.

3. EXPERIMENTAL

3.1. Sample characterization

Three model alloys based on Fe-C-Ni were studied. These alloys contained carbon between the range of 0.338 to 0.382 wt% and nickel in the range of 1.084 – 4.478 wt%. The chemical composition, determined by the GDA 750 HP optical emission spectrometer (GDOES), is listed in **Table 1**. In addition, the determination of carbon, oxygen and sulfur contents was provided by Eltra 2000 CS and Eltra 2000 ONH combustion analyzers.

Table 1 Chemical composition of studied alloys (wt%)

Alloy	C	Cr	Ni	O	P	S	Mn	Al	Cu	N
Ni1	0.382	0.010	1.084	0.002	0.004	0.006	0.030	0.010	0.014	0.003
Ni3	0.375	0.012	2.990	0.003	0.004	0.006	0.086	0.011	0.009	0.002
Ni5	0.338	0.010	4.478	0.001	0.005	0.006	0.031	0.011	0.012	0.003

The alloys were prepared from pure metals (Fe and Ni, purity 99.99 %), and carbon (purity 99.99 %) in furnace Leybold Heraeus by vacuum induction melting and cast into a cylindrical mould without additional heat treatment.

3.2. Differential thermal analysis (DTA) experiments

DTA measurements were performed for obtaining temperatures of solidus (T_S), start ($T_{P,S}$) and end ($T_{P,E}$) of peritectic transformation and liquidus (T_L). The Setaram Setsys 18_{TM} equipment with S-type thermocouples was used for experimental measurements. The samples for DTA analysis were processed into the cylindrical form of diameter 3.5 mm, height 2.8 mm and mass of 190 ± 5 mg. Before analysis, they were polished to remove surface oxides and sonicated in acetone. All measurements were carried out under the same conditions in alumina crucibles at a heating rate of 10 °C·min^{-1}. Temperature calibration of DTA was performed prior to each experiment using Pd (5 N). The influence of the heating rate and sample mass was taken into account. An inert atmosphere of argon (purity higher than 99.9999 %) was maintained during experiments.

3.3. Differential scanning calorimetry (DSC) experiments

Temperatures of phase transformations were also obtained by DSC method. The experimental measurements were made by Setaram MHTC (Multi High-Temperature Calorimeter) 96 Line with 3D heat-flux DSC sensor (B-type). The samples for DSC analysis were processed into the cylindrical form of diameter 5.0 mm, height 8.0 mm and mass of 1220 ± 5 mg. The alumina sleeves (volume 360 µl) were inserted into a platinum crucible and sealed with an alumina cover and platinum cover. The whole set was then placed on the 3D DSC sensor

and covered by the corundum cover. Empty corundum sleeve in the platinum crucible served as a reference sample. The measurements were carried out at a heating rate of 5 °C ·min^{-1}. For temperature calibration was used Pd (5N), the influence of heating rate and mass of sample was also taken into account. An inert atmosphere of helium was used. The purity of gas was higher than 99.9999 %.

3.4. Dilatometry experiments

Temperatures of phase transformations, coefficient of thermal expansion and density were determined by dilatometry. The Netzsch DIL 402 Expedis Supreme with S-type thermocouple was used for experimentally measurements. 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 container as possible in which they were analysed. Temperature calibration was performed using Pd (5N). Further, calibration for thermal expansion with use of Al_2O_3 standard and correction to a sample holder (by SW) was performed. The measurements were carried out in sapphire containers (it was also included in the corrections). The dynamic atmosphere of helium was maintained in the furnace during the analysis. The purity of helium was 99.9999 %. The heating rate was 10 °C·min^{-1}. Throughout the experiment, a static force of 0.2 N was applied to the sample.

4. RESULTS AND DISCUSSION

4.1. Temperatures of phase transformations

The phase transition temperatures were studied in the high temperature area. Temperatures of solidus, liquidus, start and end of peritectic transformation were detected by DTA, DSC method and dilatometry. Experimental values were compared and discussed with theoretical calculations obtained by SWs JMatPro and Thermo Calc (**Table 2**). **Figure 1** shows all the DTA curves and **Figure 2** shows all the dilatometric curves obtained for the analysed alloys. The DSC curves are very similar to DTA curves, therefore, they were not displayed graphically.

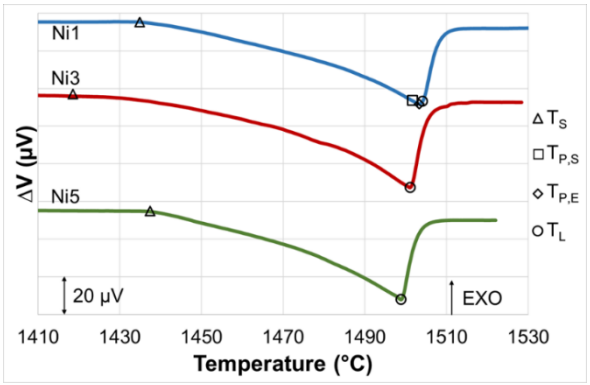

Figure 1 DTA curves of analysed alloys

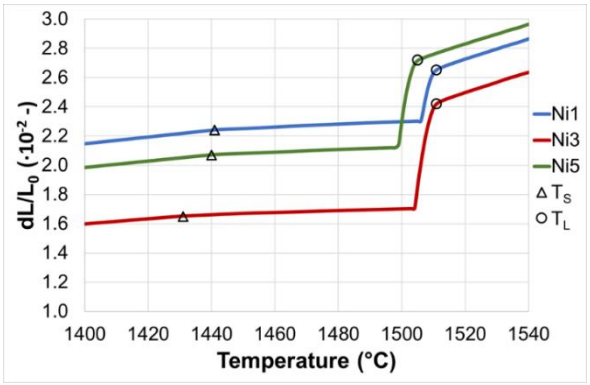

Figure 2 Dilatometric curves of analysed alloys

As the nickel content increases, the liquidus temperature for DSC and dilatometric measurements decreases. For DTA measurements, the liquidus temperature is the same for Ni3 and Ni5 samples. The smallest temperature range in which melting takes place is for Ni5 alloy and the largest is for Ni3 alloy.

It is clear from **Figure 1** that the Ni1 sample has the highest liquidus temperature and the Ni3 and Ni5 samples have a slightly lower T_L. The solid temperature is almost identical to Ni1 and Ni5 alloys, for the Ni3 sample it is lower by 14 – 16 °C. Peritectic transformation was detected only for the Ni1 sample. It took place in the range of 1 °C. It follows that nickel narrows the area of peritectic transformation, which is also confirmed by the calculations in SW Thermo-Calc.

Table 2 Experimental and theoretical values of phase transition temperatures of studied alloys (°C)

	Experiment			Calculations	
°C	DTA	DSC	DIL	TC	JMP
			Ni1		
T_S	1441	1445	1442	1451	1439
$T_{P,S}$	1492	-	-	1497	1500
$T_{P,E}$	1493	-	-	1498	1501
T_L	1496	1502	1509	1503	1502
			Ni3		
T_S	1427	1436	1429	1444	1435
T_L	1492	1500	1508	1497	1499
			Ni5		
T_S	1443	1445	1442	1445	1440
T_L	1492	1499	1503	1497	1499

The obtained experimental and theoretical results show that for the solidus temperature from the experimental results the unambiguous influence of the change of the nickel content on its shift was not determined. As the nickel content increased, the experimental and theoretical liquidus temperature decreased.

The obtained results of statistical analysis show that the differences in phase transformation temperatures in comparison with individual experimental methods are from 1 to 16 °C. The smallest deviations were recorded for T_S comparison (DTA-DIL) and the largest deviations for T_L (DTA-DIL). The differences may be due to the effects of the experimental conditions of the individual methods, the interactions of the individual elements and the kinetics of the phase transformations.

4.2. Coefficient of thermal expansion and density

The coefficient of thermal expansion and density were studied in the tempetrature range of 1000 – 1595 °C using dilatometry. All experimental data were compared with theoretical calculations obtained by SWs JMatPro and Thermo-Calc. Temperature dependence of coefficient of thermal expansion is presented in **Figure 3** and density is presented in **Figure 4**.

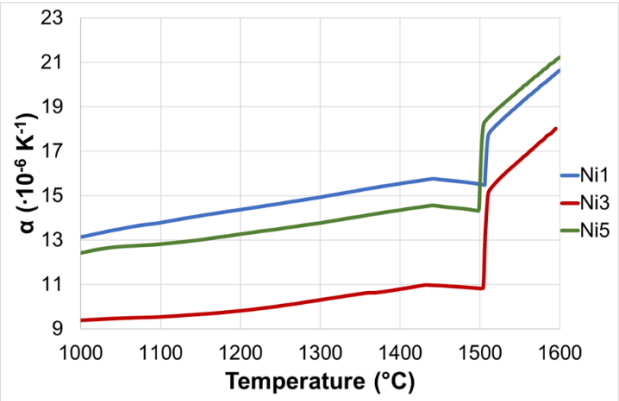

Figure 3 Temperature dependence of experimental coefficient of thermal expansion of analysed alloys

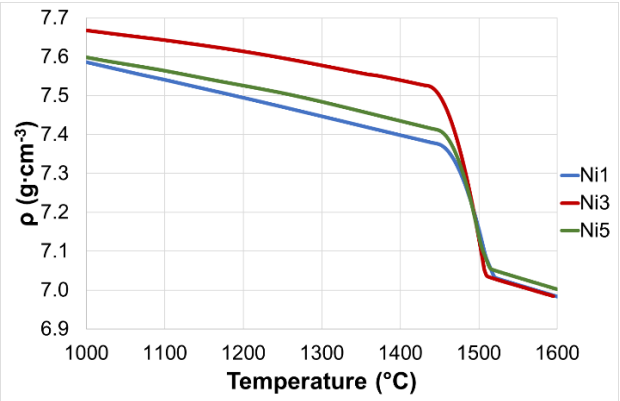

Figure 4 Temperature dependence experimental density of analysed alloys

In the temperature range of 1000 – 1400 °C are experimentally obtained values of coefficient of thermal expansion in the interval from 9.39 to 15.54·10^{-6} K^{-1}. The lowest values of *α* are for alloy Ni3 and the highest for Ni1 alloy. Calculated values by both SWs were in the interval from 12.06 to 17.45·10^{-6} K^{-1}. Calculations using both SWs had opposite trends of impact of nickel content change. According to SW JMatPro, the lowest values of α had Ni1 and the highest Ni5, which means that with increasing nickel content the values of the coefficient of thermal expansion increase. According to SW Thermo-Calc, the lowest values of the coefficient of thermal expansion had sample Ni5 and the highest values had Ni1 alloy, so with increasing nickel content the values of α decrease.

In the melting range (1400 – 1530 °C) the experimental values of the coefficient of thermal expansion are in the range from 10.80 to 19.22·10^{-6} K^{-1}. In the temperature region 1400 – 1500 °C alloy Ni3 has the lowest values of *α* and sample Ni1 has the highest values of *α*. From 1501 to 1530 °C, the alloy Ni3 has the lowest values of the coefficient of thermal expansion and the highest has alloy Ni5. During melting (1400 – 1530 °C) the calculated values of the coefficient of thermal expansion are in the range from 14.80 to 27.23·10-6 K^{-1}. The range of 1400 – 1450 °C according to the calculations of SW JMatPro with increasing nickel content the values of the coefficient of thermal expansion increase. Calculations according to SW Thermo-Calc show the opposite trend of the change of nickel content. For the temperature range 1451 – 1530 °C, it is not possible to determine a clear effect of the change in nickel content on the change in the values of the coefficient of thermal expansion.

In the liquid phase (1530 – 1595 °C) the experimental values of the coefficient of thermal expansion are from 15.98 to 21.10·10^{-6} K^{-1}. Ni3 alloy has the lowest values and sample Ni5 has the highest values. In the temperature range 1530 – 1595 °C, the calculated values of the coefficient of thermal expansion are from 27.01 to 27.77·10^{-6} K^{-1}. According to SW JMatPro, the lowest values of *α* had Ni5 alloy and the highest had sample Ni3. According to the calculations of SW Thermo-Calc, the trend of the effect of the change of nickel content was the opposite, the lowest values of the coefficient of thermal expansion had the alloy Ni3 and the highest had sample Ni5.

In the temperature range from 1000 to 1400 °C, the alloy Ni3 has the highest experimental density and the lowest has sample Ni1, range from 7.40 to 7.67 g·cm^{-3}. The calculated density is in range from 7.35 to 7.63 g·cm^{-3}. Calculations using both SWs have the same trends. Ni1 alloy has the lowest values of *ρ* and Ni5 the highest density. As a result, the density increases in this area with increasing nickel content.

In the temperature range 1400 – 1530 °C, the experimental values of density are in the range from 7.02 to 7.54 g·cm^{-3}. From 1400 to 1509 °C, the sample Ni1 has the lowest values of *ρ* and the highest has alloy Ni3. In this temperature range, with increasing nickel content, the density increases, but again this is not a clear dependence. From 1510 to 1530 °C, Ni5 alloy has the lowest *ρ* values and alloys Ni1 (1510 – 1515 °C) and Ni3 (1516 – 1530 °C) have the highest values of density. The calculated density values in the temperature range 1400 – 1530 °C are from 7.01 to 7.44 g·cm^{-3}.

In the liquid phase (1530 – 1595 °C) the experimental density values are in the range from 6.98 to 7.04 g·cm^{-3}. Ni1 and Ni3 alloys have the same values of density, which are the lowest, The Ni5 sample has higher values of density. In this area, it is not possible to determine a clear trend of the impact of the change in nickel content on the change in *ρ* values. The calculated density values are in the range from 6.95 to 7.03 g·cm^{-3}. Calculations using both software have the same trends. Ni1 alloy has the lowest values of *ρ* and Ni5 has the highest values of density. As a result, the density increases in this temperature range with increasing nickel content.

The experimental results show that in the temperature range 1000 – 1509 °C the alloy Ni1 has the minimum values of *ρ* and maximum values has alloy Ni3 or Ni5. In this temperature range, the increasing nickel content probably increases the density. According to SW JMatPro calculations, the growing nickel content increases the density in almost the entire studied temperature range, except for 1461 – 1501 °C. SW Thermo-Calc calculations have the same trend.

5. CONCLUSION

New original data concering temperatures of phase transformation in melting, coefficient of thermal expansion and density for three model alloys based on Fe-C-Ni were obtained experimentally by DTA, DSC method and dilatometry and theoretically by utilization of SW JMatPro, Thermo-Calc.

Based on the obtained results, the following conclusions can be stated:

In the case of the temperatures of melting:

For the experimental and theoretical values of solidus temperature was not detected the unambiguous influence of the change of the nickel content on its shift. The experimental and theoretical liquidus temperature decreased with increasing nickel content.

In the case of coefficient of thermal expansion and density:

With increasing nickel content decreased experimental values of thermal expansion coefficient in the whole studied temperature range. According to the results of SW JMatPro, the increasing nickel content increases the *α* values from 1000 to 1400 °C and according to SW Thermo-Calc, it decreases them. From 1401 to 1595 °C, the unambiguous influence of nickel on the change in the values of the coefficient of thermal expansion was not demonstrated for both SWs. In the temperature range of 1000 – 1509 °C with increasing nickel content increase experimentally values of density. The same trend have the theoretical values obtained by SWs JMatPro and Thermo-Calc.

The obtained results show that there are still often significant differences between experimental and theoretical values even for relatively simple systems (alloys). The high quality of experimental material data of these systems (eg Fe-C, Fe-C-Ni) is crucial for a better understanding of more complex to polycomponent systems (especially steels and related alloys).

ACKNOWLEDGEMENTS

This paper was created within the frame of the project No. CZ.02.1.01/0.0/0.0/17_049/0008399 from the EU and CR financial funds provided by the Operational Programme Research, Development and Education, Call 02_17_049 Long-Term Intersectoral Cooperation for ITI, Managing Authority: Czech Republic - Ministry of Education, Youth and Sports, and student projects SP2022/39, and SP2022/13.

REFERENCES

[1] BERNS, H., THEISEN, W. *Ferrous materials: Steel and cast iron*. Heidelberg: Springer Berlin, 2008.

[2] RANA, R. *High-Performance Ferrous Alloys*. Cham: Springer, 2021.

[3] MIETTINEN J. Calculation of solidification-related thermophysical properties for steels. *Metallurgical and Materials Transactions B*. 1997, vol. 28, no. 2, pp. 281-97.

[4] DROZDOVÁ, Ľ., SMETANA, B., PRESOLY, P., NOVÁK, V., MACHŮ, M., BERNHARD, M., et al. Investigation of Fe–C–Cr and Fe–C–Cr–Ni-based systems with the use of DTA and HT-LSCM methods. *Journal of Thermal Analysis and Calorimetry*. 2020, vol. 142, no. 2, pp. 535-546.

[5] GUR, C.H., PAN, J. *Handbook of Thermal Process Modeling Steels*. Boca Raton: CRC Press, 2008.

[6] XU, T., SONG, G., YANG, Y., GE, P.-X., TANG, L.-X. Visualization and simulation of steel metallurgy processes. *International Journal of Minerals, Metallurgy and Materials*. 2021, vol. 28, pp. 1387-1396.

[7] SAUNDERS, N., GUO, U.K.Z., LI, X., MIODOWNIK, A.P., SCHILLÉ, J.-S. Using JMatPro to model materials properties and behavior. JOM. 2003, vol. 55, pp. 60–65.

[8] ANDERSSON, J.O., HELANDER, T., HOGLUND, L., HI, P., SUNDMAN, B. Thermo-Calc & DICTRA, computational tools for materials science. *Calphad*. 2002, vol. 26, no. 2, pp. 273–312.