THERMAL ANALYSIS STUDY OF Fe-C-Ni AND Fe-C-Cr BASED SYSTEMS

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https://doi.org/10.37904/metal.2019.678

Abstract

Model alloys based on Fe-C-Ni and Fe-C-Cr with graded carbon, chromium and nickel content were studied. Two devices with various arrangements and principle of measurement were used and solidus, peritectic transformation and liquidus temperatures were precisely determined for prepared model alloys. DTA method with simultaneous thermal analyser Setaram SETSYS 18TM and dilatometry with NETZSCH DIL 402 Expedis Supreme (NanoEye) dilatometer were performed. Phase transition temperatures were studied during crossing from solid to liquid phase. Differences between experimental and theoretical temperatures in order of dozens of degrees of centigrade were observed, especially for solidus and peritectic transformation temperatures.

Keywords: DTA, dilatometry, Fe-C-Ni and Fe-C-Cr based alloys, solid and liquid phase, phase transition temperatures

1. INTRODUCTION

Concerning metals production, one of the most crucial is metals casting. Casting technologies (continuous casting, ingots casting) can be optimized by various sophistic SW applications (Procast, Magmasoft, …) [1,2] along with the knowledge of proper thermodynamical and thermophysical quantities. Some quantities can be directly used for the real technological process, e.g., a temperature of liquidus for optimal adjusting of casting temperature. By the optimization of a technological process or direct utilization of most proper data, the competitiveness can be substantially improved, the production costs can be lowered, and therefore financial profit can be increased. The knowledge of thermophysical and thermodynamical characteristics of materials is also the basis of understanding of the fundamental behaviour of materials [3]. Such information improves the prediction of behaviour and calculation of key quantities of materials and hence higher effectivity in production and development of new materials can be achieved.

At present, on the grounds of theoretical knowledge of materials and experimental study, sophisticated SW applications or computational equations [4] are used for fast and cheap materials data prediction. Among most used high-quality applications are SW Thermo-Calc [4], Dictra [4], FactSage [4], Thermodata [4], JMatPro [4] and many others [4]. Theoretical study with the utilization of mathematical modelling can be a suitable, useful, complementary and fast alternative for obtaining crucial materials data [4], but the utilization of obtained calculated data has to be performed very carefully with respect to the possibility to obtain inaccurate or even misleading data. Various approaches are applied at present, like empirical models [4] and fundamental models [5].

Despite continuously enhanced and developed SW applications, the most important way is the experimental investigation by various experimental methods [6-8]. Physical properties (viscosity of melt [9], surface properties of melt - surface tension [9], density [10], …) can be studied using sophisticated experimental equipment [6,7,11,12]. Many of physical quantities can be obtained using methods of thermal analysis [8]. These methods enable to study materials during heating, cooling, by isothermal dwell, by altering various regimes of temperature (cycling), and force impact or atmosphere under various experimental circumstances [8]. Thermophysical, thermodynamical and also kinetic behaviour of materials in solid, liquid and gas phase can be investigated under precisely defined experimental conditions.

Performed study presents solidus, peritectic transformation and liquidus temperatures of laboratory prepared Fe-C-Ni and Fe-C-Cr alloys obtained by DTA (Differential Thermal analysis) and Dilatometry compared and discussed with calculation results.

2. EXPERIMENT

2.1. Samples characterization

Two laboratory prepared alloys based on Fe-C-Ni and two alloys based on Fe-C-Cr were prepared by vacuum induction meting from pure metals (Fe, Ni, Cr) with addition of graphitic carbon. Ingots about three kilograms were cast. Alloys with various Ni and Cr contents were prepared. The chemical composition presents **Table 1**.

Table 1 Chemical composition of studied alloys /wt. %

Alloy	C	Ni	Cr	Mn	Al	N	W	P	S	O
Ni1	0.382	1.084	0.010	0.030	0.010	0.003	0.001	0.004	0.005	0.002
Ni5	0.338	4.478	0.010	0.031	0.010	0.003	0.001	0.005	0.002	0.001
Cr1	0.344	0.001	0.924	0.056	0.010	0.026	0.025	0.004	0.007	0.002
Cr5	0.340	0.001	4.760	0.042	0.004	0.001	0.044	0.002	0.003	0.001

2.2. DTA - Differential Thermal Analysis

DTA analysis samples were prepared from ingots. Rods of 3.5 mm in diameter were machined and from these rods small cylinders of a height of 3 mm were cut. Samples were brushed and cleaned in acetone by ultrasound impact. The samples mass was approximately 190 mg. DTA Setaram SETSYS 18$_{TM}$ device with S-type measurement rod and corundum crucibles were used for samples analysis. Temperature calibration (99.999 % Ni and 99.999 % Pd) and corrections with respect to the heating rate and sample mass were applied for proper phase transition temperatures determination. The dynamic high purity (99.9999 % Ar) atmosphere was maintained during analysis and three evacuating procedures were performed before starting the analysis. The heating rate used was 10 °C/min. Mean values from three runs was evaluated.

2.3. Dilatometry

Dilatometry samples were prepared from ingots also. Rods of 6.34 mm in diameter were machined and from these rods small cylinders of a height of 10 mm were cut. Samples were brushed and cleaned in acetone by ultrasound impact. The samples mass was approximately 2 400 mg. Dilatometer Netzsch DIL Expedis SUPREME NanoEye with corundum holder, push rod, sapphire ampoules and S-type thermocouple were used for samples analysis. Temperature calibration (99.999 % Ni and 99.999 % Pd) was applied for proper phase transition temperatures determination (c-DTA). The dynamic high purity (99.9999 % He) atmosphere was maintained during analysis and three evacuating procedures were performed before starting the analysis. The force applied to the sample was 0.2 N and the heating rate used was 10 °C/min. Mean values from two runs were evaluated.

3. THEORETICAL CALCULATIONS

Theoretical calculations were performed by use of sophisticated SW. IDS (Solidification analysis Package - Interdendritic Solidification, S and N not included for calc.) [13] and TC (Thermo-Calc, Sn, As, Sb, O and N not included for calc.) SW [14] were used for all three phase transition temperatures calculations. Among these two SW applications, NEM approach [4,15] was used. NEM approach is based on the calculation of transition temperatures using suitable empirical equations. The resulting phase transition temperatures are the mean values of sure count of calculated solidus, peritectic transformation and liquidus temperatures.

4. RESULTS AND DISCUSSION

Temperatures of phase transformations were obtained based on DTA and dilatometric curves analysis, see **Figures 1-4**. **Figures 1** and **2** show DTA curves of samples Ni5 and Cr5. Colored dots show solidus, peritectic transformation and liquidus temperatures ("raw" values - not corrected values). By the same evaluation procedure were obtained phase transition temperatures for other two alloys Ni1 and Cr1. Resulting phase transition temperatures present **Tables 2** and **3**.

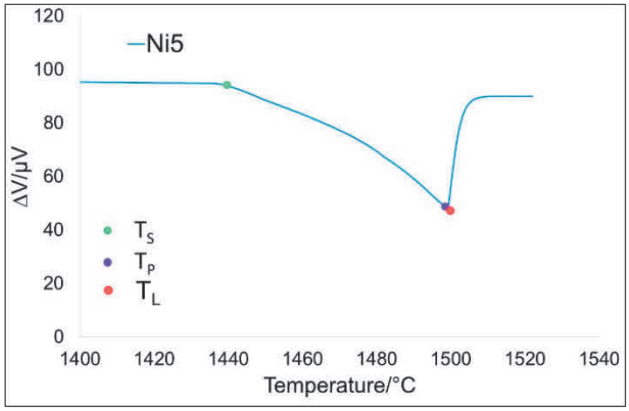

Figure 1 DTA curve of alloy Ni5, solidus temperature (T_S) - green circle, peritectic transformation temperature (T_P) - purple circle and liquidus temperature (T_L) - red circle

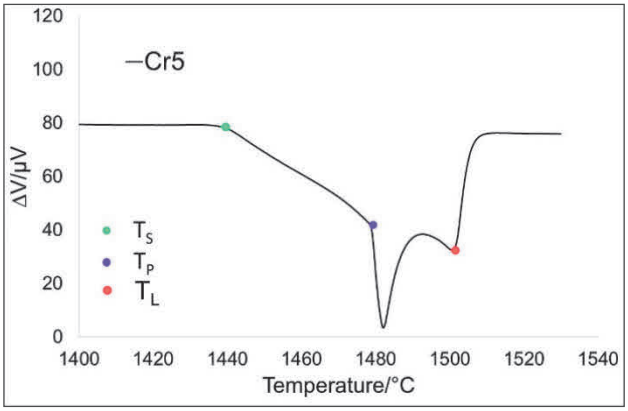

Figure 2 DTA curve of alloy Cr5, solidus temperature (T_S) - green circle, peritectic transformation temperature (T_P) - purple circle and liquidus temperature (T_L) - red circle

Figures 3 and **4** show dilatometric curves of samples Ni5 and Cr5. Colored temperatures show solidus, peritectic transformation and liquidus temperatures ("raw" values - not corrected values). By the same evaluation procedure were obtained phase transition temperatures for other two alloys Ni1 and Cr1. Resulting phase transition temperatures present **Tables 2** and **3**.

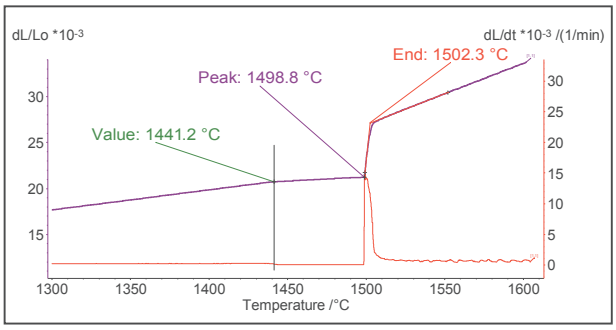

Figure 3 Dilatometric curve of alloy Ni5, solidus temperature (T_S) - green value, "peritectic transformation temperature (T_P)" - purple value and "liquidus temperature (T_L)" - red vaue

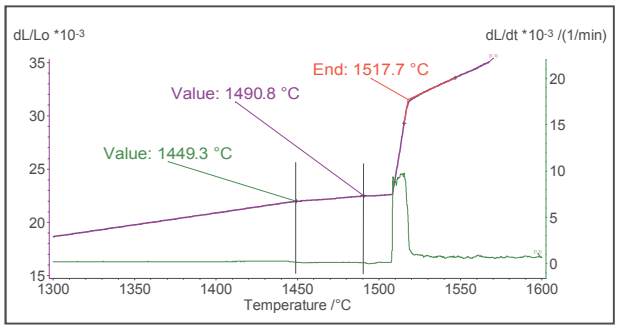

Figure 4 Dilatometric curve of alloy Cr5, solidus temperature (T_S) - green value, "peritectic transformation temperature (T_P)" - purple value and "liquidus temperature (T_L)" - red value

Peritectic transformation temperatures and liquidus temperatures are not presented for dilatometry (because of no relevant temperatures were obtained - no correction with respect to the experimental conditions performed).

4.1. Solidus temperatures

Experimental values obtained by DTA and dilatometry are very close to each other, the difference is no more than 9 °C (alloy Cr1, the worst agreement). Focused on Ni based alloys, the differences between calculated values and experimental are not so pronounced (8 and 14 °C, **Table 2**). Contrary to this fact, solidus temperatures for Cr based alloys (**Table 3**) differ substantially, the difference between experimental and theoretical values reach in the case of IDS (Interdendritic Solidification Package) SW 112 °C (Cr1) and TC (Thermo-Calc) SW 43 °C (Cr1). More pronounced difference was observed for alloy Cr5 (IDS, 174 °C) and better agreement was observed for TC and experimental values (Cr5, 15 °C).

4.2. Peritectic transformation temperatures

Peritectic transformation temperatures (DTA) and theoretical values are in better accordance for Cr based alloys, the largest difference is 15 °C. More pronounced differences were encountered for Ni based alloys, 26 °C and 45 °C. Compared to the solidus temperatures no so large differences between experimental and theoretical values were observed. Interesting is also the fact that TC SW calculated only solidus and liquidus temperatures. No peritectic transformation was the result of calculation using TC SW. It probably relates with the fact that the composition of alloy is bordering the maximum carbon content at which peritectic transformation can take place (in Fe-C-Ni ternary - pseudo ternary system). This can be supported also by experimental measurement, see **Figure 1**. Only a tiny peak (purple dot) before the top of the peak (red dot) was observed on DTA curve.

Table 2 Phase transition temperatures for alloys Ni1 and Ni5 /°C

Temperatures		DTA	DIL	IDS	TC	NEM
Sample Ni1	T_S	1445	1443	1437	1451	1453
	T_P	1496	-	1470	1451	1495
	T_L	1496	-	1502	1503	1501
Sample Ni5	T_S	1445	1443	1431	1444	1453
	T_P	1491	-	1465	-	1495
	T_L	1491	-	1496	1497	1493

Table 3 Phase transition temperatures for alloys Cr1 and Cr5 /°C

Temperatures		DTA	DIL	IDS	TC	NEM
Sample Cr1	T_S	1454	1443	1342	1411	1462
	T_P	1487	-	1489	1495	1496
	T_L	1502	-	1505	1508	1505
Sample Cr5	T_S	1445	1447	1273	1460	1459
	T_P	1473	-	1474	1481	1488
	T_L	1497	-	1499	1502	1500

4.3. Liquidus temperatures

Liquidus temperatures obtained experimentally and calculated are for Ni and also Cr based alloys very close to each other. The maximum deviation is 7 °C for sample Ni1. Very high degree of agreement was achieved for liquidus temperatures. It seems that IDS, Tehrmo-Calc and also NEM are all suitable for these phase transition temperatures calculations.

Precision of solidus, peritectic transformation and liquidus temperatures was performed using DTA. Solidus temperatures were determined also applying dilatometric measurements. For peritectic transformation and liquidus temperatures it is necessary to develop the methodology with respect to the experimental conditions (not yet performed and almost not mentioned in the accessible literature).

DTA results and dilatometric results are comparable. Very small deviations were observed. Only in the case of sample Cr1 the difference is 10 °C. It seems that dilatometric measurements can be applied for solidus temperature determination and after development of methodology also for other phase transition temperatures determination in the melting region.

The largest deviations, in order of about dozens of degrees of Celsius, between experimental (DTA) and theoretical values (IDS, TC and NEM) were observed for solidus temperatures (up to 174 °C), then for peritectic transformation and the smallest for liquidus temperatures.

Larger differences between experimental and theoretical values of solidus temperatures were observed for Cr based alloys. Larger differences between experimental and theoretical values of peritectic transformation temperatures were observed for Ni based alloys. Negligible differences between experimental and theoretical liquidus temperatures were observed for both Ni and Cr based alloys.

It seems, that from comparison of experimental and calculated data the NEM approach is more suitable than IDS and Thermo-Calc SW.

5. CONCLUSIONS

Original experimental data: solidus, peritectic transformation and liquidus temperatures were obtained using Differential Thermal Analysis and Dilatometry. Pronounced differences were observed for solidus and peritectic transformation temperatures and very good agreement was observed for liquidus temperatures. Dilatometric analysis seems to be a reliable alternative for solidus temperatures determination. Differences between results for Ni and Cr based alloys were observed. NEM approach seems to be, in some cases, more reliable for phase transition temperatures determination in comparison with IDS and TC calculations. Based on the investigation, mainly in case of solidus and peritectic transformation temperatures, substantial difference persists between experimental and theoretical data.

ACKNOWLEDGEMENTS

This work was supported in the frame of GAČR reg. no. 17-18668S project solution and students projects SP2019/90, SP2019/43 (Faculty of Materials Science and Technology) and "Support of gifted students of doctoral studies at VŠB-TUO" no.: 04766/2017 / RRC (Moravian-Silesian Region).

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