DILATOMETRY ANALYSIS 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. %. Thermal expansion coefficient and density were studied in the temperature range of 200 – 1600 °C. Temperatures of phase transformations in the low and high-temperature area were evaluated too. The experimental data were obtained using dilatometry. The NETZSCH DIL 402 Expedis Supreme with NanoEye, the optoelectrical displacement system, was used for experiments. Measurements were done in an inert atmosphere of pure helium by a heating rate of 10 °C/min. The experimental data were compared and discussed with the calculation results using SW Thermo-Calc with implemented Fe-based alloys database TCFE8.1 and SW JMatPro with implemented General steel database. The influence of various contents of chromium and nickel was studied.

Keywords: Fe-C-Cr-Ni alloys, dilatometry, thermal expansion coefficient, density, temperatures of phase transformation, Thermo-Calc, JMatPro

1. INTRODUCTION

Thermophysical and thermodynamic properties of systems based on Fe were and still are a subject of extensive research [1-3]. To predict thermophysical and thermodynamic material properties of complex systems, it is necessary, to have a high quality of experimental data of simpler systems such as Fe-C-O-Cr, Fe-C-O-Ni or Fe-C-O-Cr-Ni [4,5]. The key material data required for the thermodynamic and thermophysical description of materials include the phase transformation temperatures, thermal expansion coefficient, density and others [3,5].

Control of thermal expansion is critical issue of engineering design in a wide range of applications, especially when components are small, undergo large temperature gradients, or require high dimensional stability over a wide range of temperatures [6]. Materials with low coefficients of thermal expansion are demanded in many fields. These materials can improve the thermal stability of devices in precision measuring instrument fields, optoelectronic devices manufacturing areas and microelectronics fields [7]. Materials with specified mechanical, thermal properties and superlow thermal expansion are needed not only for rocket engineering in aviation and space industries but also for high-temperature-resistant composites with steel matrix [8]. Obtaining a low density of steel with good mechanical properties is one of the critical issues in current automotive or construction industry [9,10].

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%. 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 dilatometric analysis were processed into the form of cylinders with a diameter of 6.35 mm and 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. The samples were polished (the possible oxidation layer was removed) and cleaned by ultrasonic impact in acetone before analysis. The length calibration was performed using Al_2O_3. Temperature calibration was performed in the low-temperature area with Ag and the high-temperature area using Pd.

2.2. Experimental conditions

For obtaining the experimental results was used NETZSCH DIL 402 Expedis Supreme with 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 %.

There were experimentally obtained dilatometric curves, from which thermal expansion coefficient and density were calculated in software Proteus. Two measurements were carried out under the same experimental conditions. The force applied to the sample was 0.2 N and the heating rate used was 10 °C/min. Temperatures of phase transformations were detected from a derivation of the dilatometric curve and its c-DTA curve. In this work are presented mean values from two measurements.

3. THEORETICAL CALCULATIONS

Theoretical calculations were performed using thermodynamic SWs 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.

Both software do not calculate the thermal expansion coefficient and density directly. The thermal expansion coefficient is calculated as a function of molar volume, and density is calculated as a function of mass and volume of the system. The thermal expansion coefficient is calculated from volumetric expansion coefficient from relation [11]:

$$\beta = \frac{1}{V_0}\frac{dV}{dT} \quad (1)$$

where:

β - volumetric expansion coefficient (K^{-1}), V – volume (m^3), V_0 – initial volume (m^3), T – temperature (K)

For isotrophic materials $\beta \approx 3\alpha$ [11], where α is thermal expansion coefficient (K^{-1}).

4. RESULTS AND DISCUSSION

The thermal expansion coefficient and density in the temperature range from 200 to 1600 °C were studied for all alloys. Temperatures of phase transformations in the low and high-temperature area were detected too. Experimental values were compared with theoretical calculations obtained by SW JMatPro and Thermo-Calc. The experimental and theoretical values are presented in **Figures 1 – 4.**

4.1. Temperatures of phase transformations

Temperatures of phase transformations were detected from dilatometric curves. In **Table 2**, there are experimentally and theoretically obtained values. In **Figure 1**, there are marked temperatures of phase transitions at the experimental curves. The start of α →γ is marked as $T_{\alpha\rightarrow\gamma,S}$ and the end is marked as $T_{\alpha\rightarrow\gamma,E}$. The temperature of solidus is market as T_S, and the temperature of liquidus is marked as T_L.

From **Table 2**, can be see, that with increasing content of chromium and nickel, temperatures of phase transformations in α→γ transformation and melting are shifting to lower values. The most significant differences between experimental and theoretical values are for the start of phase transformations ($T_{\alpha\rightarrow\gamma,S}$, T_S).

This may be due to the fact that the temperatures of the onset of transformations are more difficult to determine experimentally (using thermal analysis methods). The end of the phase transformation is often more noticeable than the start, mainly in high-temperature area. Furthermore, this may be because the theoretical calculations are mostly concerned with the liquidus temperature, and therefore, there are also the smallest differences between the experimental and theoretical T_L values.

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

°C	DIL	JMatPro*	TC**
CrNi1			
$T_{\alpha\rightarrow\gamma,S}$	746	710	717
$T_{\alpha\rightarrow\gamma,E}$	783	765	766
T_S	1424	1453	1456
T_L	1510	1503	1502
CrNi3			
$T_{\alpha\rightarrow\gamma,S}$	739	658	670
$T_{\alpha\rightarrow\gamma,E}$	771	742	748
T_S	1422	1448	1451
T_L	1504	1496	1494
CrNi5			
$T_{\alpha\rightarrow\gamma,S}$	678	-	-
$T_{\alpha\rightarrow\gamma,E}$	796	722	728
T_S	1426	1432	1437
T_L	1493	1488	1485

***Calculation includes all elements**

****Elements not included for calculation: O, P, S**

The start of α →γ transformation was not calculated for CrNi5 alloy according to which the transformation proceeds from the initial temperature of the calculation (25 °C). This behavior is characteristic of duplex steels, which usually contain a higher content of chromium (over 20 wt%).

Theoretical values from JMatPro calculations are closer to experimental data. It can be caused by the fact that calculation with SW JMatPro includes all elements and calculation with SW Thermo-Calc does not include O, P, S elements.

4.2. Thermal expansion coefficient

Experimentally obtained values of thermal expansion coefficient are presented in **Figure 1**. Comparison of experimental and theoretical values was performed for all alloys. As an example, was selected CrNi3 alloy, which results are in **Figure 2**.

From the experimentally obtained dependence of thermal expansion coefficient (α) on temperature, it is clear, that alloy CrNi1 has the highest values of α in the whole temperature range. The lowest values in the temperature range of 273 – 765 °C has alloy CrNi5. From 765 °C to 1499 °C has the lowest values of α alloy CrNi3. According to calculations in SW JMatPro, α values decrease with increasing chromium and nickel content. It is not possible to determine a clear trend of thermal expansion coefficient values shift from the SW Thermo-Calc calculations.

Experimentally obtained thermal expansion coefficient is within the range of $11.34 – 14.32 \cdot 10^{-6}$ K^{-1} (200 – 680 °C), $7.88 – 14.37 \cdot 10^{-6}$ K^{-1} (681 – 900 °C), $9.7 – 14.48 \cdot 10^{-6}$ K^{-1} (901 – 1400 °C) and $13.02 – 30.12 \cdot 10^{-6}$ K^{-1} (1401 – 1600 °C).

The theoretical values from both calculations are in the range of 12.13 – 17.45 $\cdot 10^{-6}$ K^{-1}(200 – 680 °C), 6.95 – 14.44$\cdot 10^{-6}$ K^{-1} (681 – 900 °C), 9.7 – 16.53$\cdot 10^{-6}$ K^{-1} (901 – 1400 °C) and 14.06 – 27.65$\cdot 10^{-6}$ K^{-1} (1401 – 1600 °C). The smallest differences between experimental and theoretical calculations are except for phase transformations, there are in the range of 0.00 – 33.72 %. The higher differences are in the phase transformations. The biggest difference is 86.51 % for alloy CrNi3 in α→γ transformation.

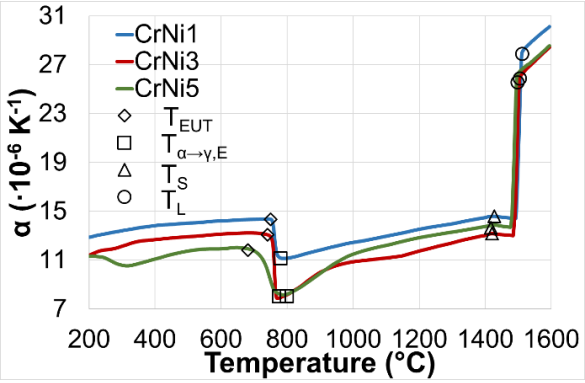

Figure 1 Experimentally obtained thermal expansion coefficient for all alloys with marked temperatures of phase transformations

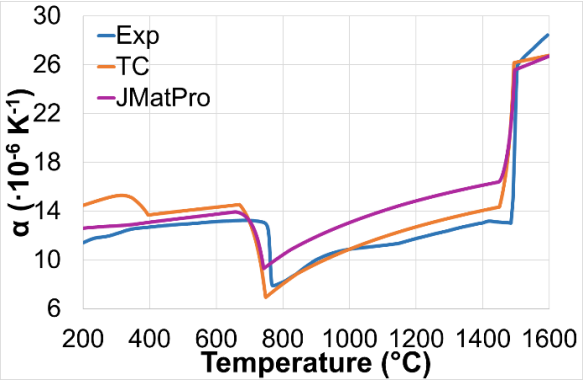

Figure 2 Comparison of experimental and theoretical data of thermal expansion coefficient for alloy CrNi3

The experimental results show that with increasing content of chromium and nickel, α shifts to lower values to α → γ transformation. After that, the CrNi3 sample has higher values than CrNi5 up to the melt.

4.3. Density

Experimentally obtained values of density are presented in **Figure 3**. Comparison of experimental and theoretical values was performed for all alloys. As an example, was selected CrNi3 alloy, which results are in **Figure 4**.

From experimentally obtained dependence of density (ρ) on temperature, it is clear, that CrNi5 alloy has the highest values to 1000 °C. In the temperature range of 1001 – 1480 °C densities of CrNi3 and CrNi5 alloy overlap. The lowest values have alloys CrNi1 and CrNi3 to 700 °C. In the temperature ranges of 701 – 1480 °C and 1517 – 1600 °C has the lowest values of density CrNi1 alloy. The calculations in the SW Thermo-Calc show that with increasing chromium and nickel content, the density values increase up to the solidus temperature. The opposite trend occurs at this temperature. Calculations in SW JMatPro show the same trend up to liquidus temperature. From this temperature, the CrNi5 sample again has the highest density values.

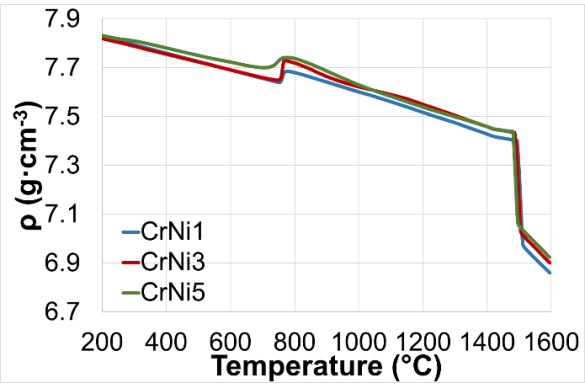

Figure 3 Experimentally obtained density for all alloys

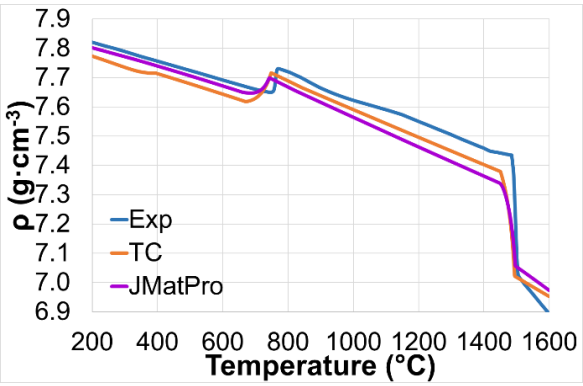

Figure 4 Comparison of experimental and theoretical data of density for alloy CrNi3

Experimentally obtained density is within the range of 7.66 – 7.83 g·cm^{-3} (200 – 680 °C), 7.64 – 7.74 g·cm^{-3} (681 – 900 °C), 7.43 – 7.69 g·cm^{-3} (901 – 1400 °C) and 6.86 – 7.46 g·cm^{-3} (1401 – 1600 °C).

The theoretical values from both calculations are in the range of 7.62 – 7.81 g·cm^{-3} (200 – 680 °C), 7.61 – 7.73 g·cm^{-3} (681 – 900 °C), 7.36 – 7.64 g·cm^{-3} (901 – 1400 °C) and 6.95 – 7.41 g·cm^{-3} (1401 – 1600 °C). The differences between experimental and theoretical calculations are very small. They are in the range of 0.00 – 4.82 %. The largest differences are in the melting for both calculations (3.37 – 4.82 %).

The experimental results show that chromium and nickel have very small effect on the change of density. With increasing chromium and nickel content, the density values increase slightly over the entire temperature range.

5. CONCLUSION

The thermal expansion coefficient and density were studied in the temperature range of 200 – 1600 °C by dilatometry. The temperatures of phase transformations in the low and high-temperature area were obtained as well. The experimental data were discussed and compared with the theoretical calculations by SWs JMatPro and Thermo-Calc. Higher differences between experimental and theoretical calculations are for thermal expansion coefficient. The most significant differences are in α→γ transformation for alloy CrNi3.Very good agreement between experimental and theoretical values was shown in the case of density (maximum deviation of 4.83%).

In the case of phase transformation temperatures, the best agreements are between the experimental and theoretical values for the temperature of liquidus. The most significant differences are in the case of the start of phase transformations ($T_{\alpha\rightarrow\gamma,S}$, T_S). These may be caused by the fact that the theoretical calculation of T_L is given the most attention; this temperature is best investigated. In the case of the beginnings of transformations, there is often a problem in their unambiguous experimental determination. The peak may be flattened, with a slow onset of phase transformations.

With increasing chromium and nickel content, the values of the thermal expansion coefficient decrease. In the case of density, the opposite is true. The CrNi5 sample has the highest values of density.

Values of thermal expansion coefficient obtained by measurement are valuable as input data for computational modelling of processes involving heating or cooling of steel products or semi-products during manufacturing, especially for designing or optimizing of production technology. Another usage is in products designing with specified properties in various fields like construction, automotive or aerospace industry.

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