

THERMODYNAMIC APPROACH TO THE INVESTIGATION OF THE SURFACE TENSION OF STEELS

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Abstract

In the presented work, evaluation and further investigation of previously derived thermodynamic approach for calculation of surface tension of steel was done. Surface tension of pure iron and real steel grades was measured using the sessile drop method up to 1600 °C. Also, surface tension of iron and steels was calculated using thermodynamic approach. Furthermore, calculated and measured values of surface tension were compared and good agreement with difference cca 10 % (and better) was found. Thermodynamic quantities, which are necessary for this thermodynamic approach, were calculated using Thermo-Calc 2015b software with TCFE8 database.

Keywords: Surface tension, steel, Thermo-Calc, thermodynamic quantities

1. INTRODUCTION

Steel research is still highly topical theme [1, 2]. Properties of steels can be obtained by experimental techniques [3] and nowadays also using theoretical modelling [4]. Due to the increasing number of papers focused on theoretical modelling, new models and approaches are developed [5] and these model/approaches have to be verified [6].

A lot of models and/or approaches are available for the calculation of surface tension. Butler equation [7] is the most commonly used model for surface tension calculations, another commonly used models are Kohler model [8], Toop model [9] and Chou model [10]. These models require information of subsystems as input [11] and these data are usually incomplete [12] or data mentioned in literature differ [13, 14].

Our, previously described approach [15] used in this study, needs only knowledge of thermodynamic quantities of the alloy and experimental value of surface tension of standard at one temperature. Input thermodynamic quantities can be obtained experimentally [16] or these quantities can be obtained using specific software. In this work, all required thermodynamic quantities of steels were calculated using Thermo-Calc 2015b [17] with TCFE8 database.

2. EXPERIMENTAL CONDITIONS

Surface tension was measured using sessile drop method [10]. Samples (pure iron and two steel grades) were machined into cylindrical shape with 5 mm diameter and 5 mm length. Surface tension was measured up to 1600 °C under inert atmosphere of pure argon (6N), heating rate was set to 5 K·min⁻¹ from 25 °C to 1470 °C. Heating rate from 1470 °C to 1600 °C was set to 2.5 K·min⁻¹.

Most important [18] and significantly presented elements in investigated steel samples are in **Table 1**. In addition to both steel samples, surface tension of pure iron was measured.

Table 1 Most important and significantly presented elements of steel samples (wt. %)

Sample	C	O	S	N	Mn	Si	Cr
1	0.162	0.0019	0.007	0.0076	0.71	0.19	0.05
2	0.290	0.0019	0.007	0.0038	0.81	0.21	0.61

3. CALCULATIONS

3.1. Thermodynamic approach

According to Equation (1) [15], surface tension can be calculated using thermodynamic quantities of sample.

$$\sigma_{(calc)} = \left(\frac{\partial G}{\partial A} + S \frac{\partial T}{\partial A} - V \frac{\partial p}{\partial A} \right)_n, \quad (1)$$

where $\sigma_{(calc)}$ ($\text{mN}\cdot\text{m}^{-1}$) is surface tension, G ($\text{J}\cdot\text{mol}^{-1}$) is Gibbs energy, A (m^2) is surface area, S ($\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$) is entropy, T (K) is thermodynamic temperature, V (m^3) is volume, p (Pa) is pressure and n (mol) is total amount of substances.

As there are many factors affecting experiments (i.e. wettability [19], used atmosphere) and these factors cannot be easily described by mathematical formulas, it is necessary to use scale factor f . This factor represents the ratio between calculated and experimental values of the surface tension (2) of standard:

$$f = \frac{\sigma_{(calc, std)}}{\sigma_{(exp, std)}} \quad (2)$$

where $\sigma_{(calc, std)}$ ($\text{mN}\cdot\text{m}^{-1}$) is surface tension of standard calculated using equation (1) and $\sigma_{(exp, std)}$ ($\text{mN}\cdot\text{m}^{-1}$) is experimentally measured surface tension. Surface tension of sample is then recalculated using scale factor from equation (2) and calculated value of surface tension from equation (1) according to equation (2):

$$\sigma_{(result, f)} = \frac{\sigma_{(calc, sample)}}{f} \quad (3)$$

where $\sigma_{(calc, sample)}$ ($\text{mN}\cdot\text{m}^{-1}$) is surface tension of sample calculated using equation (1) and $\sigma_{(result, f)}$ ($\text{mN}\cdot\text{m}^{-1}$) is the resulting value of surface tension of sample.

3.2. Thermo-Calc

All thermodynamic quantities from equation (1), namely Gibbs energy, entropy, thermodynamic temperature, volume and pressure, were calculated using Thermo-Calc 2015b software with TCFE8 (Thermo-Calc Fe-based alloys) database [20].

Because investigated thermodynamic approach is derived for constant amount of substances, only one phase (liquid) was allowed in calculations. Also, some elements, which are not defined in used database (i.e. Sn) were not included in calculations. Pressure in calculations was set to one atmosphere.

4. RESULTS AND DISCUSSION

4.1. Pure iron

First of all, temperature dependence of surface tension of pure iron was experimentally measured and calculated using Equations (1) - (3). Experimental value of surface tension of standard (iron), which is necessary in Equation (2), at 1560 °C was $\sigma_{\text{Fe}, 1560\text{ °C}} = 1700 \text{ mN}\cdot\text{m}^{-1}$. Comparison of calculated and measured temperature dependence of surface tension is given at **Figure 1**.

Calculated and measured values of surface tension are in very good agreement and both have decreasing temperature dependence of surface tension. Slightly steeper temperature dependence for measured surface

tension of pure iron might be caused by traces of oxygen [21] and/or other impurities in measured sample of iron.

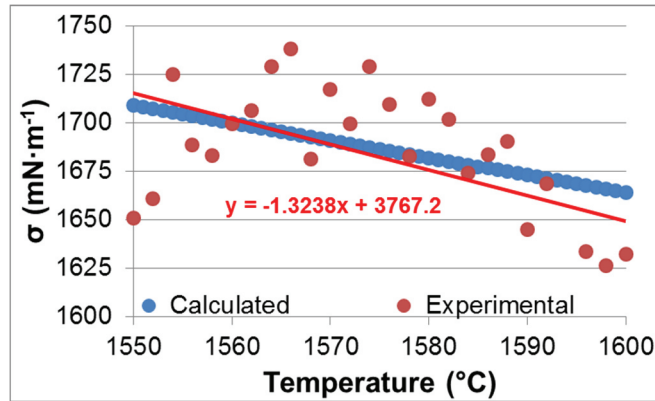


Figure 1 Comparison of calculated and measured temperature dependences of surface tension σ of iron. Measured values are smoothed by linear regression (light red)

4.2. Steel samples

Because results obtained for iron are very good and the differences between smoothed (linear regression, **Figure 1**) and calculated values are up to $20 \text{ mN}\cdot\text{m}^{-1}$, temperature dependence of surface tension of steel grades was measured under same conditions as for iron. Also, temperature dependences of surface tension of steel samples were calculated using equations (1) to (3). Same experimental value of surface tension of iron at $1560 \text{ }^\circ\text{C}$ ($\sigma_{\text{Fe},1560 \text{ }^\circ\text{C}} = 1700 \text{ mN}\cdot\text{m}^{-1}$) was used for scale factor. Comparison of measured and calculated values of surface tension are shown in **Figure 2**.

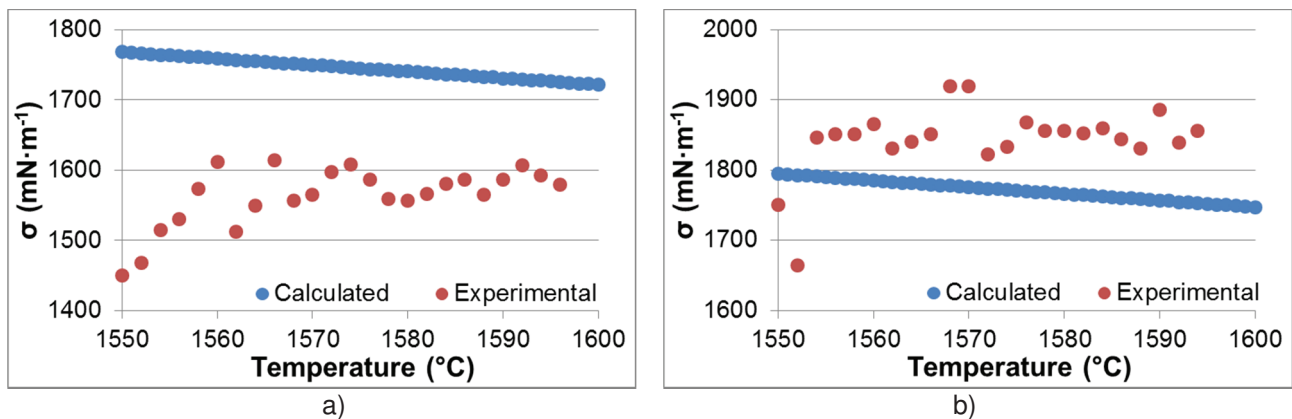


Figure 2 Comparison of calculated and measured temperature dependences of surface tension σ of
a) sample 1 and b) sample 2

Obtained experimental and calculated values of surface tension are in good agreement with published data [22]. Temperature dependence of the surface tension is linear [23, 24] and calculated temperature dependence of surface tension has the same trend.

Calculated temperature dependence of surface tension for sample 1 is a bit higher than measured temperature dependence. The difference between calculated and measured values is $\sim 150 \text{ mN}\cdot\text{m}^{-1}$ except for “the coldest part” of investigated temperature region. For sample 2, experimental temperature dependence of surface tension is a bit higher than calculated values. Measured and calculated values are close to each other, the difference $\sim 50 \text{ mN}\cdot\text{m}^{-1}$.

Experimentally measured values are mainly affected by interaction between corundum pad and steel samples [25]. Calculated values are mainly affected by phase setting (only liquid allowed) and incomplete chemical composition (exclusion of Sn). In addition of these major influences, there were probably other effects that affected measurements and/or calculations.

Both calculated dependences have slightly decreasing trend while experimentally measured dependences shows constant trend. Traces of some solid particles (oxides, sulphides, etc.) should be in investigated temperature region and these were neglected in calculations.

4.3. Scale factor

Used thermodynamic approach utilizes a single-point calibration, so the scale factor is same in the whole temperature range. However, values of surface tension are changing with temperature, so the scale factor might be also changing with temperature. For investigation of this potential influence of temperature, experimental values of surface tension of iron at different temperatures were used for calculation of scale factors and values of surface tension.

The “unsmoothed” values of surface tension includes all unwanted influences connected with experimental measurements and values “smoothed” by linear regression of measured temperature dependence of surface tension (**Figure 1**). Linear regression was used due to the linear dependence of surface tension on temperature [23]. Obtained values of surface tension and corresponding scale factors are given in **Table 2**.

Table 2 Values of surface tension σ of iron and corresponding scale factors at different temperatures T

T (°C)	1550	1560	1570	1580	1590	1600
σ (mN·m ⁻¹) ¹	1651	1700	1717	1712	1645	1632
σ (mN·m ⁻¹) ²	1715	1702	1689	1676	1662	1649
f ¹ (-)	0.1786	0.1726	0.1699	0.1695	0.1755	0.1760
f ² (-)	0.1720	0.1724	0.1728	0.1732	0.1737	0.1741

¹ values “unsmoothed”

² values according to regression line from **Figure 1**

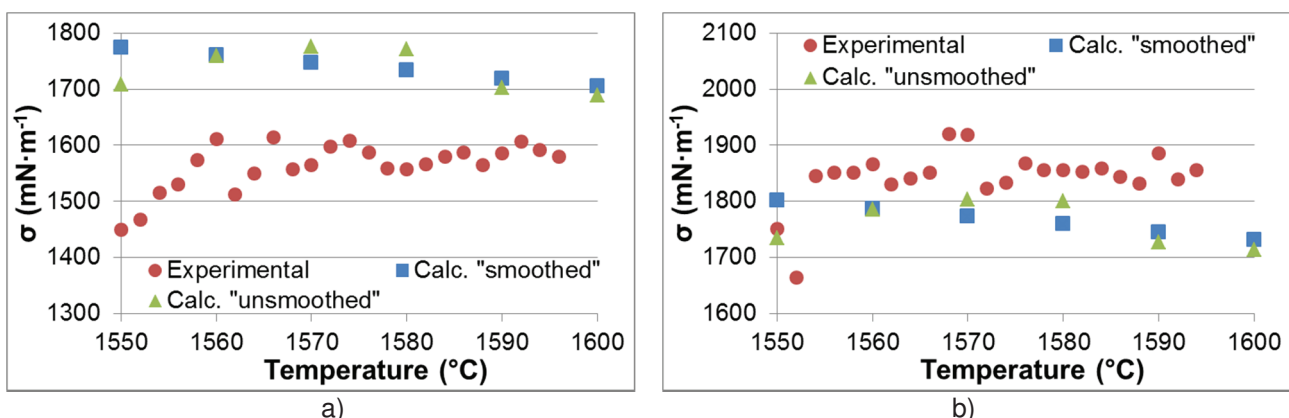


Figure 3 Measured surface tension (red), calculated surface tension obtained using scale factors from “unsmoothed” values of surface tension (green) and calculated surface tension obtained using scale factors from “smoothed” values of surface tension (blue) of a) sample 1 and b) sample 2

Then, temperature dependences of surface tension of both steel samples were calculated using the scale factors obtained with the use of surface tension of iron at these six temperatures. Obtained temperature dependences of surface tension were compared to each other and also with experiments (**Figure 3**).

Scale factor seems to be very little (if at all) dependent on temperature. The size of measurement error, which can be reduced using linear regression, affects calculated values of surface tension much more than temperature. It seems that there is no eligible temperature for calculations of scale factor. For correct calculations, it is appropriate to use experimental value of surface tension which is a little as possible affected by experimental measurement error.

CONCLUSIONS

Thermodynamic approach for calculation of surface tension was investigated in temperature range up to 1600 °C. For pure iron and two steels, approach gives temperature dependence of surface tension, which is similar to experimentally measured dependence.

Scale factor, which is necessary for investigated approach, seems to be very little dependent on temperature. Scale factor is very sensitive to quality of experimental value of surface tension of standard. It is suitable to measure standard and samples under the same conditions and it is strongly recommended to use value of surface tension of standard with (almost) no unwanted influences connected with experimental measurements for scale factor.

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