CALCULATION OF SURFACE TENSION OF REAL STEEL GRADES AT 1550 °C

KALUP Aleš[1], ŘEHÁČKOVÁ Lenka[1], ZLÁ Simona[1,2], KAWULOKOVÁ Monika[1,2],
SMETANA Bedřich[1,2]

[1] *VSB-Technical University of Ostrava, Faculty of Metallurgy and Materials Engineering, Department of Physical Chemistry and Theory of Technological Processes, Ostrava, Czech republic, EU*
[2] *VSB-Technical University of Ostrava, Regional material science and technology centre, Ostrava, Czech Republic, EU*

Abstract

In the presented work, new thermodynamic approach based on basic thermodynamics was used for calculation of the surface tension of steel. Surface tension was calculated for three steel grades and calculated values were compared with experimental values at 1550 °C. Thermodynamic properties, which are necessary for this thermodynamic approach of surface tension, were calculated using Thermo-Calc software with TCFE7 database.

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

1. INTRODUCTION

The surface properties of liquids and melts have attracted much more interest both physicist and metallurgists from the long past to the present day because of either scientific or technological importance [1-6]. During the soldering, brazing, sintering and dying, the knowledge of surface properties of the liquid state is required. Although there are a large number of methods to determine the surface properties of liquids such as surface tension, those suitable for liquid metals are limited by their chemical reactivity and high melting points [7].

In the past, many models were derived for the calculation of the surface tension [8]. Butler equation [9] is the most commonly used model for surface tension calculations, another commonly used models are Kohler model [10], Toop model [11] and Chou model [12]. In contrast to the above models, input data for our proposed approach are thermodynamic properties of the sample and experimental value of surface tension of standard. Input thermodynamic properties, such as Gibbs energy [13], can be obtained experimentally [14] or these properties can be obtained using specific software. In this work, all required thermodynamic properties were calculated using Thermo-Calc 4.0 with TCFE7 database.

2. SURFACE TENSION MODEL

Surface tension is thermodynamically defined using the partial derivative of the Gibbs energy (1) [15]:

$$\sigma = \left(\frac{\partial G}{\partial A}\right)_{T,p,n} \tag{1}$$

where σ [N·m^{-1}] is surface tension, G [J] is Gibbs energy, A [m^2] is surface, T [K] is thermodynamic temperature, p [Pa] is pressure and n [mol] is amount of substances. As it is not possible to maintain a constant temperature, it is necessary to express Gibbs energy by the first and second laws of thermodynamics (2) - (5):

$$dG = dU - d(TS) + d(p \cdot V) \tag{2}$$

$$dU = T \cdot dS + dW \tag{3}$$

$$dW = -p \cdot dV + \sigma \cdot dA \tag{4}$$

where *U* [J] is internal energy, *S* [J/K] is entropy and *W* [J] is work. Combining of equations (1) - (4) can be obtained final equation (5) for calculation of surface tension:

$$\sigma_{(calc)} = \left(\frac{\partial G}{\partial A} + S\frac{\partial T}{\partial A} - V\frac{\partial p}{\partial A}\right)_n \tag{5}$$

Equation (5) is derived for a constant amount of substances, so it can be used only for fully melted materials (above temperature of liquidus), where it is possible to assume minimal (if any) changes in phase composition (see end of section 4).

3. CALCULATIONS

All thermodynamic properties from equation (5), namely Gibbs energy, entropy, thermodynamic temperature, volume and pressure, were calculated using Thermo-Calc 4.0 [16] with TCFE7 (Thermo-Calc Fe-based alloys) database [17].

The only one quantity that must be obtained by another way is the surface of system. Material tends to minimalize its surface (more precisely, the surface energy) with a given volume. Sphere has the smallest surface with a given volume, so this shape can be used for computing the surface from its volume (6):

$$\mathrm{A} = (36\pi)^{\frac{1}{3}} \cdot \mathrm{V}^{\frac{2}{3}} \tag{6}$$

During experiments, many factors (i.e. wettability [18], effect of inert atmosphere) act to the sample, so the sample has shape different from ideal sphere. These effects cannot be 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 (7) of standard:

$$\mathrm{f} = \frac{\sigma_{(\mathrm{calc,std})}}{\sigma_{(\mathrm{exp,std})}} \tag{7}$$

where $\sigma_{(\mathrm{calc,std})}$ [$\mathrm{N \cdot m^{-1}}$] is surface tension of standard calculated using equation (5) and $\sigma_{(\mathrm{exp,std})}$ [$\mathrm{N \cdot m^{-1}}$] is experimentally measured surface tension. Surface tension of sample is then recalculated using scale factor from equation (7) and calculated value of surface tension from equation (5) according to equation (8):

$$\sigma_{(\mathrm{result,f})} = \frac{\sigma_{(\mathrm{calc,sample})}}{\mathrm{f}} \tag{8}$$

where $\sigma_{(\mathrm{calc,sample})}$ [$\mathrm{N \cdot m^{-1}}$] is surface tension of sample calculated using equation (5) and $\sigma_{(\mathrm{result,f})}$ [$\mathrm{N \cdot m^{-1}}$] is the resulting value of surface tension of sample.

4. RESULTS AND DISCUSSION:

Three industrial-grade stainless steels (samples 1-3) and two standards (pure iron and Fe-20 wt. % Ni alloy) were used to validate suggested approach. Chemical composition of samples is given in **Table 1**.

Table 1 Chemical composition of steel samples (wt. %)

Sample	C	Cr	Ni	S	Mn	Al	O	Fe
1	0.067	18.24	8.15	0.002	1.77	0.001	0.0057	bal.
2	0.056	18.28	8.20	0.009	1.80	0.001	0.0090	bal.
3	0.045	16.49	0.30	0.003	0.48	0.001	0.0164	bal.

Experimental values of surface tension at 1550 °C were obtained from literature [19] for both standards and for three real steel grades. Experimental values of surface tension of both standards are given in **Table 2**.

Table 2 Surface tension of standards at 1550 °C (N·m^{-1})

Standard	$\sigma_{(exp)}$
Fe	1.670
Fe-20 wt. % Ni	1.489

All needed thermodynamic properties of standards and samples were calculated using Thermo-Calc software with TCFE7 database. This software allows calculations only in the equilibrium state and also allows adding and excluding phases in these calculations. In this paper, only default setting with no changes in phase addition/exclusion was used (the "black box" mode) [20].

Surface tension for both standards was calculated and scale factors were obtained. These scale factors were used to calculation of surface tension of presented steels and obtained values of surface tension are given in **Table 3**. Values $\sigma_{(Fe)}$ are obtained with the use of f_{Fe} (pure iron as a standard), values $\sigma_{(Fe20Ni)}$ are obtained with the use of f_{Fe20Ni} (Fe-20 wt. % Ni alloy as a standard). Experimental values of surface tension of samples $\sigma_{(exp)}$ are given in **Table 3**.

Table 3 Surface tension of samples at 1550 °C (N·m^{-1})

Sample	$\sigma_{(exp)}$	$\sigma_{(result)}$	
		$\sigma_{(Fe)}$	$\sigma_{(Fe20Ni)}$
1	1.354	1.265	1.296
2	1.320	1.342	1.376
3	1.472	1.526	1.565

Surface tension calculated with iron as a standard are always lower than values calculated with Fe-20 wt. % Ni alloy as a standard. For sample 1, calculated surface tension is lower than experimentally measured surface tension. For samples 2 and 3, surface tension calculated with iron as a standard are closer to experimental values than surface tension calculated with Fe-20 wt. % Ni alloy as a standard.

The difference between measured and calculated surface tension is always below 0.1 N·m^{-1}. The highest difference (0.093 N·m^{-1}; standard deviation is 6.32 %) is for sample 3 with the Fe-20 wt. % Ni alloy as a standard, the lowest difference (0.022 N·m^{-1}; standard deviation is 1.67 %) is for sample 2 with pure iron as a standard. The correlation between calculated and experimental surface tension is given in **Fig. 1**.

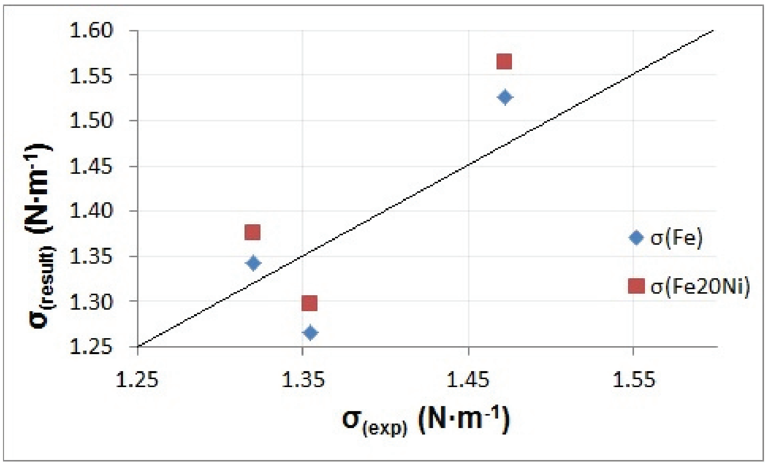

Fig. 1 Correlation between calculated and experimental values of surface tension

Calculated values of surface tension are in very good agreement with experimental results. The relative small difference between measured and calculated values of surface tension may be caused by trace amounts of other elements which have not been determined.

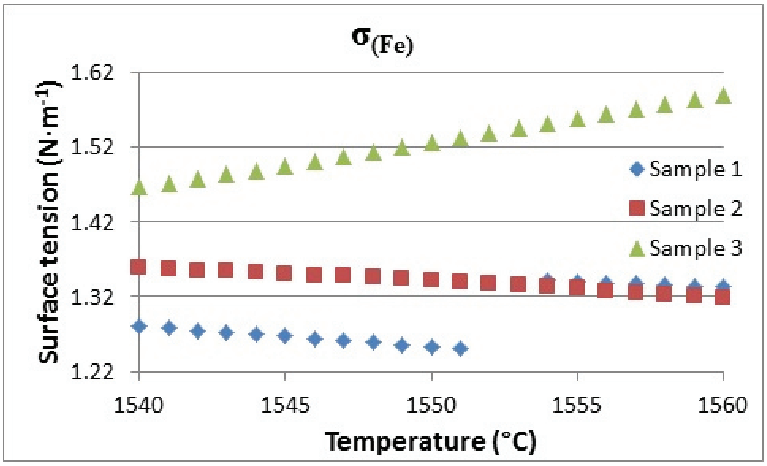

Fig. 2 Calculated surface tension (pure iron as standard)

Temperature dependence of surface tension is always continuous, so this approach has to respect it. For this reason, surface tension was calculated from 1540 °C to 1560 °C (**Figs. 2 and 3**). Samples 2 and 3 have continuous temperature dependence of calculated surface tension. For sample 1, there is small gap at 1552 °C. This gap is caused by changes in the amount of substances (disappearing of traces of MnS in this case) at this temperature.

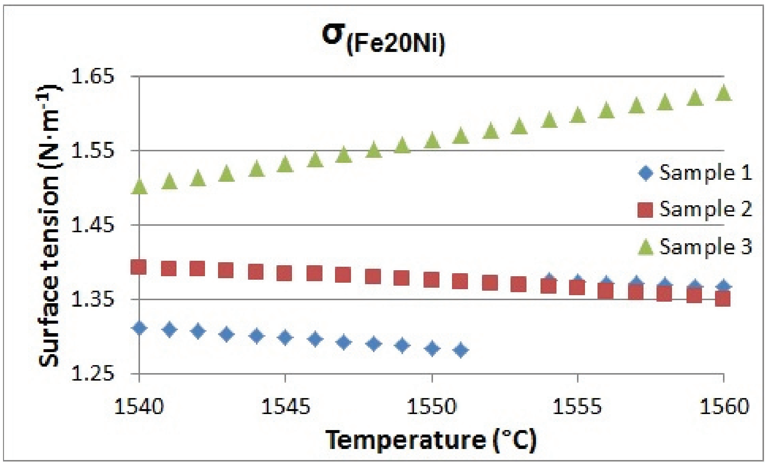

Fig. 3 Calculated surface tension (Fe-20 wt. Ni alloy as standard)

5. CONCLUSIONS

New thermodynamic approach based on classical thermodynamics for computing of the surface tension was derived and tested using three real steel grades. Approach gives values that are in a very good agreement with experimentally obtained values of surface tension. Two different materials (pure iron and Fe-20 wt. % Ni alloy) were used as standards and values calculated according f_{Fe} and f_{Fe20Ni} are close to experimental values.

Because of the use of scale factor in these calculations, the standard has to be measured under the same conditions as samples and the standard has to behave on the similar way, should have similar properties. Also, it is highly recommended to use standard with similar properties to measured material.

ACKNOWLEDGEMENTS

This paper was created on the Faculty of Metallurgy and Materials Engineering (FMME) in the Project No. LO1203 "Regional Materials Science and Technology Centre - Feasibility Program" funded by Ministry of Education, Youth and Sports of the Czech Republic. This work was also supported by two SGS projects (SP2015/88 and SP2015/70).

REFERENCES

[1] [FOWLER R. H. Proceedings of the Royal Society of London A 159 (1937) 229

[2] KIRKWOOD J. G., BUFF F. P. Journal of Chemical Physics 17 (1949) 338

[3] LANG N. D., KHON W. Physical Review B 1 (1970) 4555

[4] EVANS R. Journal of Physics C 7 (1974) 2808

[5] MAHAN G. D. Physical Review B 12 (1975) 5585

[6] ZYKOVA-TIMAN T., CERESOLI D., TARTAGLINO U., TOSSATI E. Physical Review Letters 94 (2005) 176105

[7] KORKMAZ S. D., KORKMAZ S. Applied Surface Science 257 (2010) 261-265

[8] TANAKA T. Treatise on Process Metallurgy: Process Phenomena 2 (2014) 35-59

[9] PICHA R., VŘEŠŤÁL J., KROUPA A. Calphad 28 (2004) 141-146

[10] YAN L., ZHENG S., DING G., XU G., QIAO Z. Calphad 31 (2007) 112-119

[11] PLEVACHUK Y., SKLYARCHUK V., GERBETH G., ECKERT S., NOVAKOVIC R. Surface Science 605 (2011) 1034-1042

[12] ROSYPALOVA S., ŘEHÁČKOVÁ L., DUDEK R., DOBROVSKÁ J., DOBROVSKÝ Ľ., ŽALUDOVÁ M. Proceedings of the 22nd International Conference Metallurgical and Materials Conference, Metal, 2013, Brno, Czech Republic, p. 80-85

[13] COTES S., GUILLERMET A. F., SADE M. Materials Science and Engineering A273-275 (1999) 503-506

[14] BANERJEE A., RAJU S., DIVAKAR R., MOHANDAS E. Materials Letters 59 (2005) 1219- 1222

[15] MEYBODIA M. K., SHOKROLLAHIB A., SAFARIB H., LEEC M., BAHADORID A. Chemical Engineering Research and Design 95 (2015) 79-92

[16] ANDERSSON J. O., HELANDER T., HÖGLUND L., SHI P. F., SUNDMAN B. Calphad 26 (2002) 273-312

[17] Thermo-Calc Software TCFE7 Steels/Fe-alloys database version 7, (Accessed 23 Aug 2013)

[18] TANAKA T., LEE J., SCHELLER P. R. Treatise on Process Metallurgy: Process Phenomena 2 (2014) 61-77

[19] SHARAN A., CRAMB A. W. Metallurgical and Materials Transactions B 26B (1995) 87-94

[20] KALUP A., ŽALUDOVÁ M., ZLÁ S., DROZDOVÁ Ľ., SMETANA B. Proceedings of the 23rd International Metallurgical and Materials Conference, Metal, 2014, Brno, Czech Republic, p. 695-700