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MODELING OF SURFACE PROPERTIES OF METALLURGICAL SOLUTIONS: STEELS, SLAGS AND STEEL-SLAG SYSTEMS

MODELOWANIE WŁASNOŚCI POWIERZCHNIOWYCH ROZTWORÓW METALURGICZNYCH: STALE, ŻUŻLE I UKŁADY STAL-ŻUŻEL

The aim of the study was elaboration of a model for prediction of the surface properties of such metallurgical solutions like steels, slags and for steel/slag interfaces for broad range of chemical compositions of the phases and temperatures. There have been carried out the following steps: (i) constructing of the data base for the systems in question, (ii) working out the program for establishing of the equilibrium conditions (chemical compositions) for metal/slag systems, (iii) elaboration of the computer programs for prediction of surface tensions for the systems as follows: metal/gas, slag/gas and metal/slag. The models, constructed by the authors, allow to present results in form of either model equations, Excel sheets or graphic plots.
Keywords: modeling, surface tension, interfacial tension, steels, slags, interfaces

Celem artykułu było opracowanie modelu dla prognozowania właściwości powierzchniowych roztworów metalurgicznych takich jak stale, żużle oraz układu metal/żużel dla szerokiego zakresu składów chemicznych faz oraz temperatur. Przeprowadzono następujące kroki: – opracowano bazę danych w układzie pytań, – opracowano program do ustalania warunków równowagowych (skład chemiczny) dla układu metal/żużel, – opracowano program do prognozowania napięcia powierzchniowego dla układów takich jak: metal/gaz, żużel/gaz, metal/żużel. Zaproponowany model pozwolił na oszacowanie napięcia powierzchniowego w zakresie od 30 do 85 mN/m, przy standardowym zakresie odchylenia. Model opracowany przez autorów pozwala na zaprezentowanie uzyskanych wyników w postaci innych równań modelowych, arkuszy Excela oraz wykresów graficznych.

Introduction

Significance of surface phenomena for steel production is particularly crucial for such processes like removal of inclusions from molten metal, slag spreading on metal, filtration of metals and slag penetration into refractory or foaming in arc furnace process. In particular, the surface tension data for those systems which allow to predict the direction of the heterogeneous reactions are lacking. As there is no sufficient supply of the experimental data, the modeling based on statistical analysis seems to be the best way at the current.

1. Data base

The surface tension data for pure liquid metals, binary, ternary and more-component iron-base solutions (cast iron, austenitic and ferritic steels), pure liquid metal oxides and two- and more-component oxide solutions (slags) as well as the interfacial tension data for metal/slag systems were collected. The data were set in the form of tables, model equations and graphs with respect to the concentrations (activities) of the components and temperature. Usually, the data were produced on the base of the graphic plots taken from the literature by using digitalization techniques. The architecture of the data base was customized to the system analysis of the effect of different factors on the surface properties. It was based on the Excel application which allows for query and basic statistics. The base confined the following elements: components' contents (wt% and mole%) with attributed identification number, temperature of a measurement (°C and °K), surface tensions data, measurement methods, ambient gas phase (air, argon, helium or other gas), authors' names, bibliographic data of the report and a credibility assessment. Additionally, the computation of a control sum for the component contents and the introduction of the code of the operator was provided.

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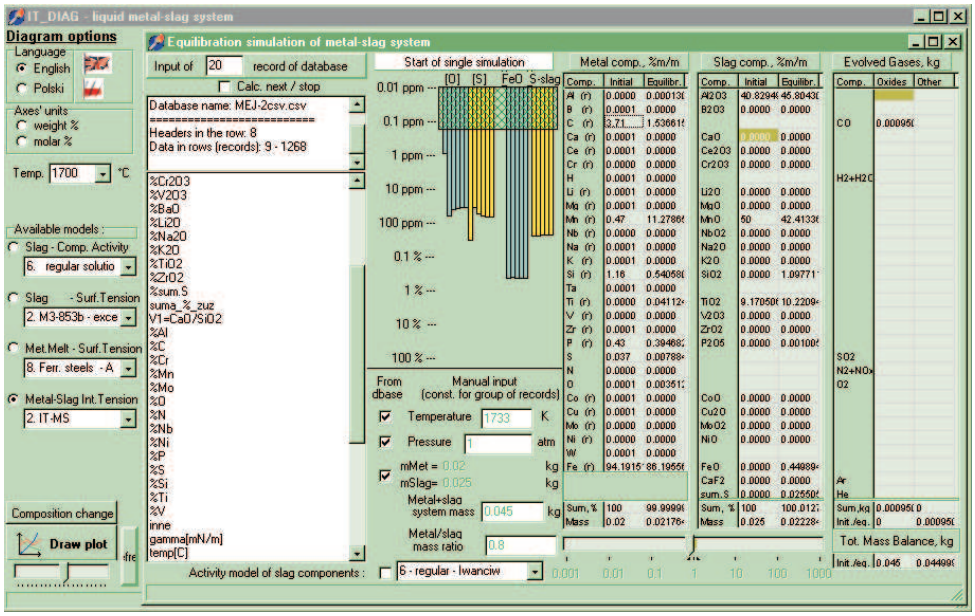

Fig. 1. The exemplary presentation of the metal/slag equilibrium calculation program

A number of up to 27 components could be considered for each solution. Besides, a program for setting of the fitting coefficients as well as for the visualization for multi-component systems at different temperatures was operative.

The analysis of the literature data, performed by the authors, indicated a substantial scattering of the surface data reported by different investigators as well as a lack of a more precise chemical analysis information. Particularly, the lack of such data like the oxygen or sulphur content of the solutions may affect negatively subsequent statistical analyses. Therefore some averaging procedures were to be applied, sometimes based on an arbitrary approach.

2. Program for establishing of the equilibrium conditions for metal/slag systems

A special program for setting of the equilibrium conditions for metal/slag systems was designed. It allowed to determine the equilibrium contents of the components for either phase at any imposed temperature. This way it was possible to estimate the oxygen or sulphur concentrations, which often were not reported by the authors despite of the fact that they have dominant effect on the surface property. The worked-out program subjects the input data - which are in a form of the components' contents and the temperature - to a processing operation leading to establishing of the real equilibrium of the studied two-phase systems. Thus produced data are subsequently subjected to final statistical analysis. The exemplary presentation of the results is illustrated in Fig. 1.

3. Program for estimation of the surface tension for two- and more-component iron solutions

On the base of the statistical analyses, a set of the model equations – Eq.1-3 – was derived. The equations allow to predict the surface tension data as a function of the components' contents in iron-base solutions. Due to extremely high surface activities of sulphur and oxygen – which impact strongly the surface tension data – a Szyszkowski term was introduced into the model equations which allow for realistic description of the solutions' surface properties.

The master model equation included the following terms coming from the first rule preconditions:

$$\sigma(mN/m) = \sigma_{Fe} - A(T - 1823) - RT\Gamma_S 10^3 \ln[1 - K_S a_S), \quad (1)$$

σ – the surface tension of Fe solution, σ_{Fe} – the surface tension of Fe(l) at 1823K, $A(T-1823)$ – the temperature effect term, T – absolute temperature, A is negative, which makes σ decreasing with increasing temperature as expected, $RT\Gamma_S\ 10^3\ln[1\text{-}K_S a_S]$ – the Szyszkovski composition effect term, R – universal gas constant, Γ_S – the excess saturated surface concentration of a surfactant, K_S – the equilibrium absorption constant for the surfactant, a_S – the chemical activity of the surfactant.

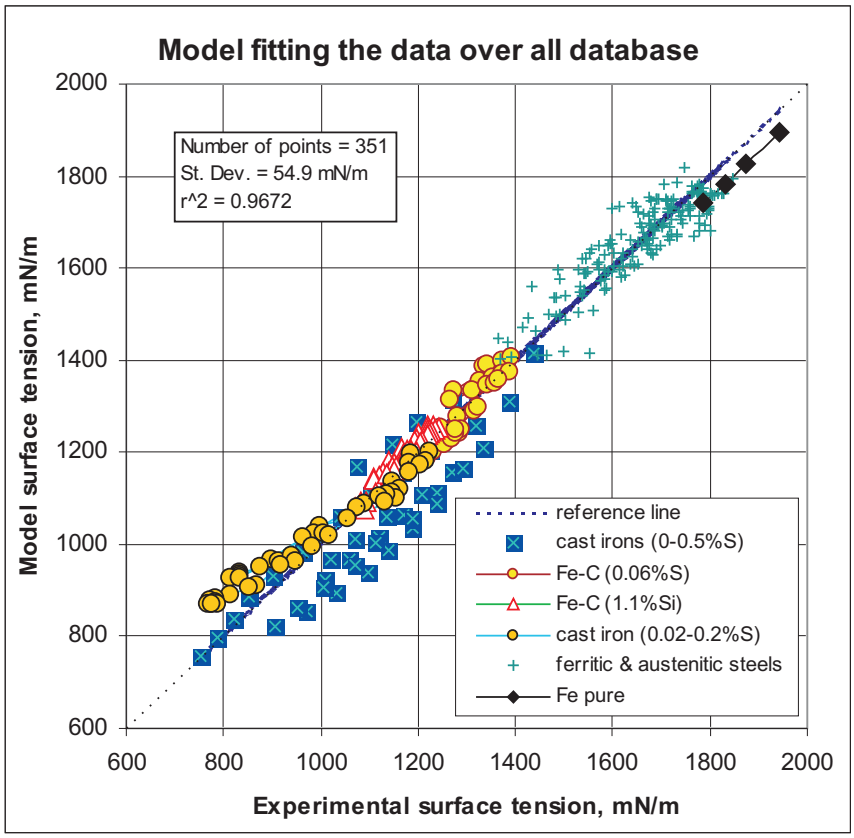

Fig. 2. Comparison of the model and experimental surface tension data for iron solutions

Based on Eq. 1, there were derived the following formulae for the iron solutions confining ferritic steels, austenitic steels and cast irons as the functions of the concentrations of the components (Eq. 2) or their chemical activities (Eq. 3):

$$\begin{aligned}\sigma\ [mN/m] \ = \ & 2674.7 - 0.43\ T - (0.05918 \\ & +0.006035\ \ [\%C])\ T \ln(1 + \exp(\tfrac{26300}{T} - 7.2)\ [\%S]) \\ & -0.011306 T \ln(1 + \exp(\tfrac{49500}{T} - 19.4)\ [\%O]) \\ & -0.0007096\ T \ln(1 + \exp(\tfrac{31000}{T} - 7.5)\ [\%C]),\end{aligned} \tag{2}$$

$$\begin{aligned}\sigma(mN/m) = \ & 2699 - 0.43T - (0.07236 \\ & +0.004895\ [\%C])\ T \ln[1 + \exp(\tfrac{19800}{T} - 7.25)\ a_S] \\ & -0.0165\ T\ \ln[1 + \exp(\tfrac{50000}{T} - 19)\ a_O] \\ & -0.0121\ T\ \ln[1 + \exp(\tfrac{46000}{T} - 10)\ a_C],\end{aligned} \tag{3}$$

where: a_O, a_C, a_{Si} – –the chemical activity of oxygen, carbon and silicon, respectively (in wt %)

The standard deviation of the model data was within ca 55 mN/m. The comparison of the model and experimental surface tension data for iron solutions is presented in Fig. 2.

4. Program for estimation of the surface tension for two- and more-component oxide solutions (slags)

For prediction of the surface tension for two- and more-component oxide solutions (slags) – depending on the components' contents of slags – an excess model formulated by Eq. 4 was applied:

$$\sigma = \sum_i (\sigma_i^o + T d\sigma_i/dT) \cdot X_i + \sum_i \sum_{j \neq i} \alpha_{i,j} \cdot X_i X_j \tag{4}$$

where: σ – the surface tension of the slag, mN/m, σ_i^0 – the extrapolated surface tension of "i" component at 0^0K, $d\sigma_i/dT$ – the temperature coefficient of the surface tension of „i" component,
$\alpha_{i,j}$ – the interaction parameters, T – temperature in K, X_i, X_j – the mole fractions of the slag components.

In Tab. 1, a fragment of the matrix of the coefficients for the considered model is presented for the 10 components most frequently met in iron metallurgy.

TABLE

A fragment of the matrix of the coefficients for the considered model for the most frequently met in iron metallurgy 10 components

i	Al_2O_3	CaO	FeO	MgO	MnO	Na_2O	P_2O_5	SiO_2	TiO_2	CaF_2
σ_i^0	768.40	614.9	–199.2	298.0	1147.9	433.3	80.8	446.9	482.3	–883.7
$d\sigma_i/dT$	–0.0558	0.0116	0.4568	0.1158	–0.2777	–0.0814	–0.0380	–0.0944	–0.0546	0.6910
Parameters $\alpha_{i,j}$										
j \ i	**Al2O3**	**CaO**	**FeO**	**MgO**	**MnO**	**Na2O**	**P2O5**	**SiO2**	**TiO2**	**CaF2**
Al_2O_3		–619.19	332.68	–726.74	–784.68	–1211.33	3.25E+10	63.246	–1495.46	–665.545
CaO			–243.10	784.07	–2500.88	–191.407	–25899.6	4.081	–869838	–569.458
FeO				–867.95	–170.15	–2029.73	–3233.78	–166.89	–152.46	–523.607
MgO					–4142.2	–30.9893	1.09E+10	481.56	–5.6E+08	913.82
MnO						–17214.5	208476.5	–288.022	–272.456	10977.1
Na_2O							1.29E+11	1694.93	1.23E+09	–3834.77
P_2O_5								17040.95		6.8E+08
SiO_2									–65.7082	-961.592
TiO_2										–6.8E+08
CaF_2										

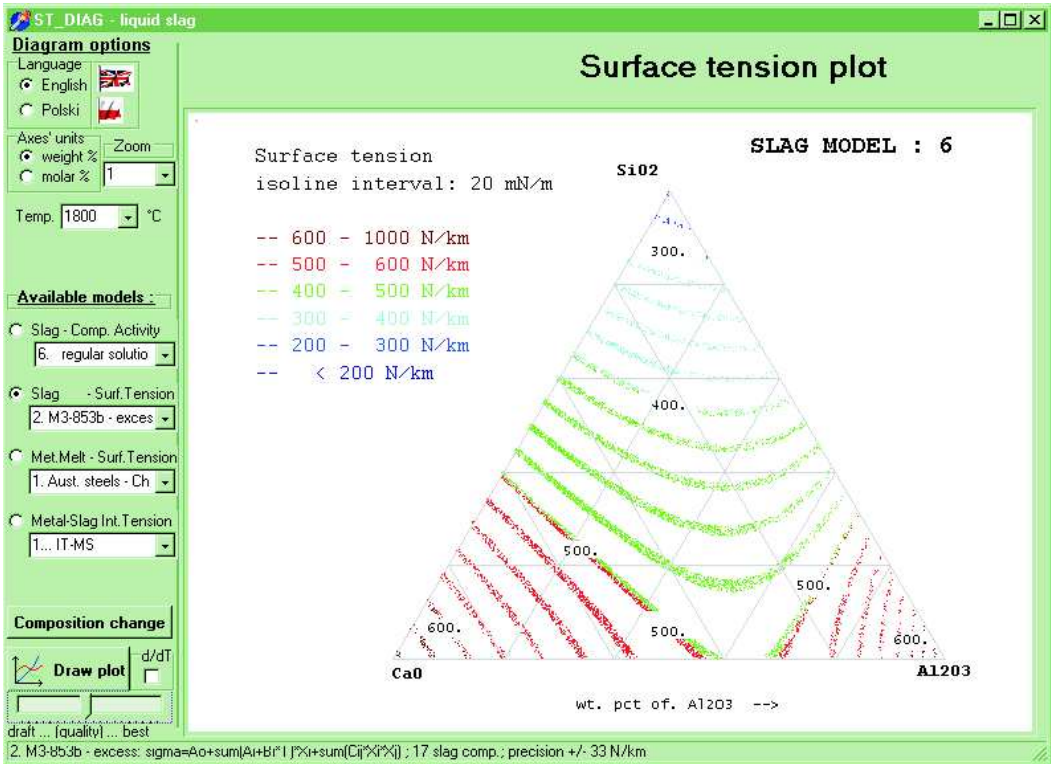

Fig. 3. The exemplary presentation of the results for slag systems

The standard deviation was of 33 mN/m, R^2= 0.955, for a number of 853 surface tension data for the slags composed of up to 17 components.

The exemplary presentation of the results for slag systems is illustrated in Fig. 3.

5. Program for estimation of the interfacial tension for steel/slag systems

For prediction of the interfacial tension for steel/slag systems a model equation – based on the Girifalco-Good approach with varying fitting parameters – was used [5].

$$\sigma_m - \sigma_{m/s} = -\sigma_s + 2\Phi(\sigma_m * \sigma_s)^{1/2} \quad (5)$$

where: σ_m the surface tension of the metal phase computed from our analytical formula, $\sigma_{m/s}$ the interfacial tension taken from the experimental data, Φ- the Girifalco-Good fitting parameter, σ_s the surface tension of the slag phase computed from our regression formula established on the base of 750 reported data points for slags. It is a complex formula considering 38 variables (simple and complex).

The program's operation consisted of the following steps: (i) input of the chemical compositions of the steel and the slag phase, (ii) setting of the equilibrium components' contents by using a special algorithm presented above in Chapter 2., (iii) substitution of the equilibrium data for each phase into the model equations, (iv) selection of the best model equation from the applied model approaches: Girifalco-Good, Szyszkowski, regression or other specific for the individual systems considered by application of the minimum standard deviation criterion to compare the experimental and the model data.

Then the fitting interaction parameter Φgas established by gtatistical regression computations:

$$\begin{aligned} 2{<}\sigma_s^{1/2} &= 585.06 - 0.30335\mathrm{T[K]} \\ &+0.2122\%\mathrm{FeO} + 143.0415\%\mathrm{Fe_2O_3} \\ &+53.6515\%\mathrm{Cr_2O_3}3.8361\%\mathrm{TiO_2} \end{aligned} \quad (6)$$

For the slags with no TiO_2, Cr_2O_3 and Fe_2O_3 the best fit may be obtained when taking

$$\Phi = 0.7167 + 0.003927\%FeO \quad (7)$$

or

$$\Phi = 0.7167 + 0.3537X_{FeO} \quad (8)$$

When using above formulae one may obtain the standard deviation close to 170 mN/m. Much better results are obtained when using other regression models. For instance, for a multi-variable model (243 variables) the standard deviation was about 84 mN/m (Fig.5), while for a linear model (31 variables) it was of 134 mN/m.

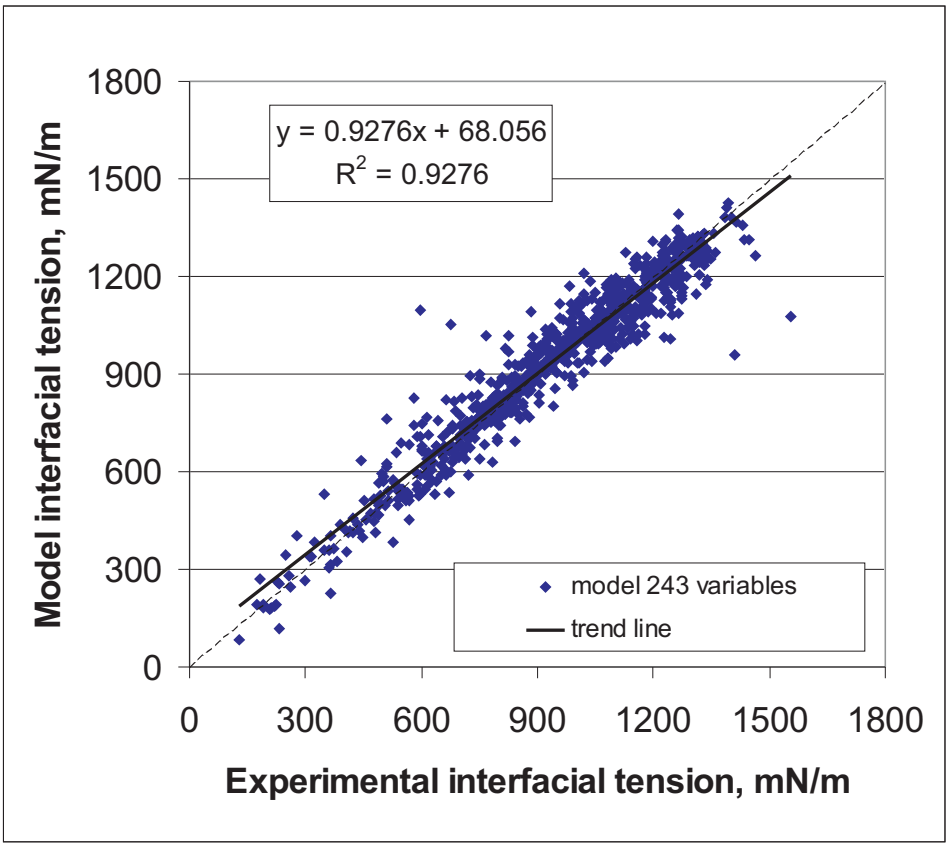

Fig. 4. Model interfacial tension versus experimental data

6. Valuation of the models

When designing the models for the interfacial tension, based on Girifalco-Good approach, there had been used the earlier ones referring to slag-gas and metal-gas systems. By using the statistical analysis methods, the variation of the Girifalco-Good coefficient, Φ, as a function of the components' contents and temperature was established. This way, a set of the optimal coefficients recommended for predictions was created.

On the base of the gathered interfacial tensions data for different metal-slag systems in a number of 841 sets, allowing for 19 components of slag phase and 13 components of metal phase, together with the temperature term, there were derived the statistical models' formulae either in linear or non-linear form (logarithms from Szyszkowski's approach).

A part of the literature information has been discarded due to its lack of a precise chemical composition data or temperature data so only 757 sets were applied for modeling of metal-slag systems.

There was also elaborated a special program designed for valuation of credibility of the chemical compositions of the literature data. It allowed to compute the equilibrium compositions and then to compare them to the literature data. This way it was possible to complete the composition data which was of a particular importance for such strong surfactants like sulphur and oxygen. Moreover, the above data processing gave some idea how far the literature data were from the equilibrium.

7. Conclusions

The performed investigations allowed for the qualitative and quantitative conclusions.

The surface tension of the iron solutions (steels) is affected mainly by such intensive surfactants like oxygen and sulphur, while typical metallic components like, for instance, Ni, Cr, Co as well as C and Si are there of a limited impact. For a particular case when the oxygen content is below 5 ppm., it is the sulphur which dominantly determines the surface tension quantity. For the oxygen content higher than 5 ppm., either the oxygen or the sulphur contribute to the surface property.

As to the slag solutions it was found that - for pure oxides - the highest surface tension levels exhibit the alkali oxides like CaO, MgO, MnO, FeO and Cr_2O_3, while the lowest ones – the acid oxides like P_2O_5, V_2O_5, MoO_3. Any addition of an oxide of a low surface tension into an oxide of a high surface tension effects eventually in a drop of the total surface tension of the solution. The low surface tension is due to the formation of large anions like VO_4^{3-}, PO_4^{3-},SiO_4^{4-} and their chain or ring polymers.

As to the interfacial tension for metal/slag systems, it was found that it is predominantly set by the metal phase while the effect of the slag phase is secondary. Analogously, like for the metal-gas systems, the interfacial quantity is strongly dependent on surface and oxygen content.

For iron solutions, the standard deviation of the model data was within 55 mN/m.

For slag solutions, the standard deviation was of 33 mN/m. For metal/slag systems the interfacial tension is within 170 mN/m when usig Girifalco-Good approach. Much better results are obtained when using other regression models. For instance, for a multi-variable model (243 variables) the standard deviation was about 84 mN/m (Fig.5) , while for a linear model (31 variables) it was of 134 mN/m.

The models, constructed by the authors, allow to present results in the form of either model equations, Excel sheets or graphic plots. Further progress in modeling of the surface properties for metallurgical systems depends to much extent on a supply of new, more precise experimental surface tensions data to fill the lacking gaps.

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