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# Equation to estimate the surface tensions of stainless steels

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Surface tension ($\gamma$) data for both austenitic and ferritic stainless steels have been analysed to derive an equation which will apply to the surface tensions of all stainless steels. It was assumed that the Al content was sufficient to hold the soluble oxygen content down to 5 ppm. The surface tensions of stainless steels can be expressed in terms of two variables, temperature and wt% sulphur:

$$\gamma(\text{mNm}^{-1}) = 1840 - 0.4(T - 1823) - 0.056T\text{Ln}\left\{1 + e^{\frac{28798}{T} - 8.5647}(0.68\%\text{S})\right\}$$

The calculated surface tensions were found to be within 3% of the measured values and values for the temperature dependence (d$\gamma$/d$T$) values were similar to the measured data.

## 1. Introduction

Surface tensions ($\gamma$) have an important effect on various processes (e.g. variable weld penetration in TIG/GTA welding [1, 2] and on the purity of single crystals produced by the floating zone method [3]) Furthermore, the surface tension of the metal phase ($\gamma_m$) is the largest factor affecting the interfacial tension ($\gamma_{ms}$) between the liquid metal and slag phases [4]. In the continuous casting of steel the interfacial tension is important since it determines the shape of the meniscus and hence the oscillation mark depth [5] and is important in avoiding slag entrapment [6].

It is important to note that the surface tensions of metals are different from other physical properties since they are dependent on the surface composition and not upon the bulk composition. Consequently, surface active elements, such as oxygen or sulphur, can have a marked effect on the surface tension even though they are only present in ppm levels. One consequence is that when a measurement of surface tension is carried out on an alloy it refers solely to that composition (i.e. for the specific O, S contents) and does not apply to (i) a different batch of the alloy or (ii) to a measurement under a different partial pressure, of $O_2$ ($Po_2$). However, compositions of alloys do change from cast to cast and thus it is necessary to have some rule or model to be able to extrapolate surface tension measurements to other compositions.

There are several types of stainless steels; they can be classified in terms of microstructure into austenitic, ferritic and martensitic stainless steels. According to the AISI numbering system, 300 and 600 series alloys have an austenitic microstructure whereas 400 series alloys have either ferritic or martensitic microstructures. All stainless steels contain Cr (usually >12%). However, 400 series stainless steels contain little or no Ni which stabilises the austenite phase. Some stainless steels contain low levels of Mo, Ti and Nb. Typical compositions of the different types of stainless steels are shown in Table I. Since the surface tension is related to the liquid phase, the nature of the solid phases (e.g. austenite, ferrite etc.) has no influence on the surface tension. However, it is influenced by the nature of the surface and in particular by the concentrations of the surface-active species such as O and S present in the surface layer. It is the *soluble* O and S (denoted $\%\underline{O}$ and $\%\underline{S}$, respectively) which affects the surface tension since the *combined* O (i.e. oxide) has little effect on the surface tension. The soluble $\underline{O}$ content is dependent upon the other alloys (e.g. Al) present in the steel (see the Fe-M-O system in Fig. 1). The aluminium content in stainless steels is deliberately kept at a low level but is typically around 0.05% (500 ppm) and it can be seen from Fig. 1 that this corresponds to a soluble $\underline{O}$ of about 4 or 5 ppm.

Several workers have reported surface tensions for various stainless steels e.g. 304 and 316 types [7–9] and 430 type stainless steels [10]. Since the surface tensions of pure Fe, Cr and Ni are very similar, differences in the concentrations of these elements in various steels are unlikely to have a large effect on the surface tension of the "clean" metal (i.e. zero O + S). Furthermore, since the concentrations of Mo and Nb (which have higher surface tensions than Fe) are relatively low, it follows

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TABLE I Typical compositions for different types of stainless steels (%) and values of the surface tension of pure metal using model [11]

| AISI Type | C max | Mn max | Si max | Cr range | Ni range | Other elements | $\gamma_{\text{pure}}$ 1823 K | $\gamma_{\text{pure}}$ 1923 K |
|---|---|---|---|---|---|---|---|---|
| | | | | Austenitic | | | | |
| 302 | 0.15 | 2.00 | 1.00 | 17.0–19.0 | 8.0–10.0 | | 1793 | 1746 |
| 303 | 0.15 | 2.00 | 1.00 | 17.0–19.0 | 8.0–10.0 | 0.60Mo(max) | 1793 | 1746 |
| 304 | 0.08 | 2.00 | 1.00 | 18.0–20.0 | 8.0–10.5 | | 1791 | 1744 |
| 310 | 0.25 | 2.00 | 1.50 | 24.0–26.0 | 19.0–22.0 | | 1768 | 1723 |
| 316 | 0.08 | 2.00 | 1.00 | 16.0–18.0 | 10.0–14.0 | 2.0–3.0Mo | 1784 | 1738 |
| 317 | 0.08 | 2.00 | 1.00 | 18.0–20.0 | 11.0–15.0 | 3.0–4.0Mo | 1797 | 1750 |
| 321 | 0.08 | 2.00 | 1.00 | 17.0–19.0 | 9.0–12.0 | Ti: $5C_{\min}$ | 1793 | 1745 |
| 347 | 0.08 | 2.00 | 1.00 | 17.0–19.0 | 9.0–13.0 | Nb: $10C_{\min}$ | 1792 | 1745 |
| 660 | 0.08 | 2.00 | 1.00 | 13.5–16.0 | 24.0–27.0 | a | 1793 | 1747 |
| | | | | Precipitation-Hardened | | | | |
| 631 | 0.09 | 1.00 | 1.00 | 16.0–18.0 | 6.50–7.75 | 0.75–1.50Al | 1777 | 1730 |
| | | | | Ferritic | | | | |
| 430 | 0.12 | 1.0 | 1.0 | 16.0–18.0 | | | 1805 | 1756 |
| 446 | 0.20 | 1.50 | 1.0 | 23.0–27.0 | 0.25max | | 1788 | 1740 |
| 434 | 0.12 | 1.0 | 1.0 | 16.0–18.0 | 0.75–1.25 | | 1804 | 1755 |
| | | | | Martensitic | | | | |
| 410 | 0.15 | 1.00 | 1.00 | 11.5–13.5 | | | 1812 | 1763 |
| 420 | 0.15 | 1.00 | 1.00 | 12.0–14.0 | | | 1812 | 1763 |
| 416 | 0.15 | 1.25 | 1.00 | 12.0–14.0 | | b | 1810 | 1760 |

Maximum S and P contents are usually 0.03% and 0.045% respectively.
a: 0.35Al, 0.001–0.010B, 1.0–1.5Mo,1.90–2.35Ti, 0.10–0.50 V.
b: 0.060%max P, 0.15%min S.

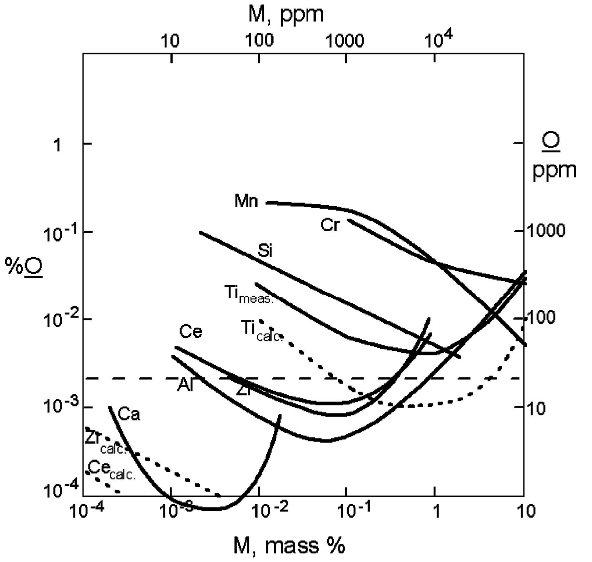


*Figure 1* Soluble oxygen (%$\underline{O}$) as a function of metal (M) concentration in Fe-M-O systems [2] at 1873 K.

that these elements also have little effect on the surface tension of the pure metal. The surface tensions of the stainless steels at 1823 and 1923 K containing no O or S ($\gamma_{\text{pure}}$) were calculated using the model due to Su *et al.* [11]. The results are given in Table I and it can be seen that the variations are small (± <1.5% around mean).

The objective of this study was to determine an equation which would cover the surface tensions of all types of stainless steels in terms of the temperature $T$ (K) and the $\underline{S}$ content (since the $\underline{O}$ content can be assumed to be fixed at ca. 4 or 5 ppm by the Al present).

## 2. Database

Brooks *et al.* [7] used the levitated drop method to determine the surface tensions for a temperature range centred around 1973 K for a large number of austenitic 304 and 316 alloys with varying S contents (Fig. 2 and Equation 1). Surface tensions at other temperatures were calculated using Equations 2 and 3.

$$\gamma_{1973}(\text{mNm}^{-1}) = 1150\text{–}90.9\ln(\%\text{S}) \tag{1}$$

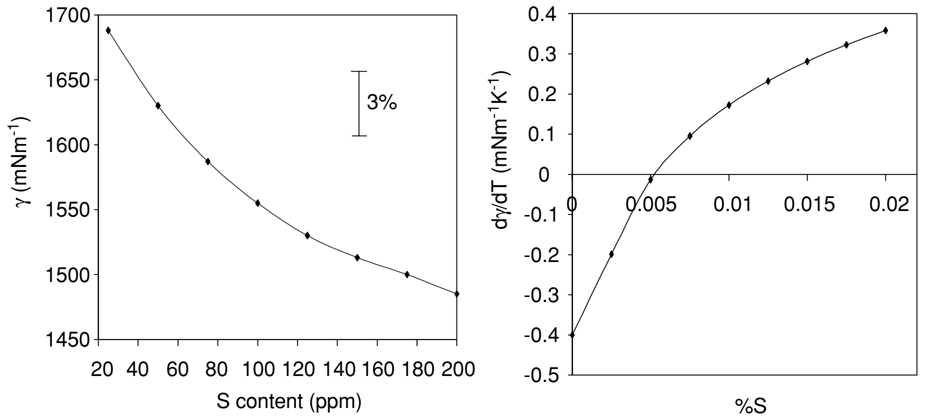
$$(\mathrm{d}\gamma/\mathrm{d}T)(\text{mNm}^{-1}\,\text{K}^{-1}) = 1.51 + 0.268\ln(\%\text{S}) \tag{2}$$

$$\gamma(T)(\text{mNm}^{-1}) = \gamma_{1973} + (\mathrm{d}\gamma/\mathrm{d}T)_{1973}(T - 1973) \tag{3}$$

where $\gamma_{1973}$ is the surface tension at 1973 K, $\gamma(T)$ is the surface tension at temperature $T$, %S is the S content of the steel.

Li *et al.* [10] used the sessile drop method to measure the surface tensions of nine ferritic 430-type stainless steels (Fig. 3) over a relatively short temperature range (1780–1880 K). These alloys contained oxygen (22 to 64) ppm and sulphur (8–105) ppm. The desired mass of sulphur was also added to the alloys to determine the effect of sulphur content on both the surface tension ($\gamma$) and temperature dependence of the surface tension ($\mathrm{d}\gamma/\mathrm{d}T$).

Experimental uncertainties associated with the different methods for determining surface tension are probably of the order of 3–5%.



(a) (b)

*Figure 2* (a) Surface tension ($\gamma$) and (b) temperature dependence ($d\gamma/dT$) of 304 and 316 stainless steels as functions of S contents [7].

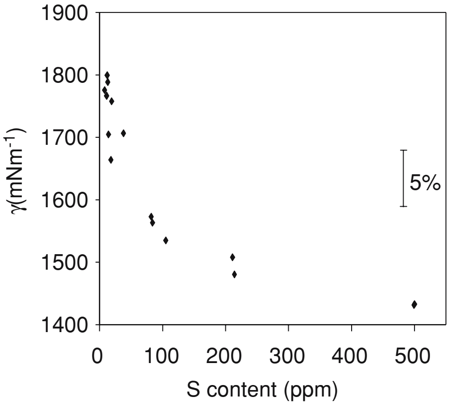


*Figure 3* Surface tension of 430 stainless steels as a function of S content [10] at 1823 K. Other surface tension values have been reported by Seetharaman [8] and Vinet [9].

## 3. Analysis of data

### 3.1. Assumptions

1. Differences in surface tension for different types of stainless steel containing no O or S ($\gamma_{pure}$) are negligible (see Table I).

2. The Al concentrations hold the calculated soluble $\underline{O}$ levels for 1873 K to 5 ppm and are independent of temperature over the range (1773–1973 K).

### 3.2. Methods used

Belton [12] reported that the effect of surface active species on the surface tension could be represented in the form of Equation 4:

$$\gamma_{pure} - \gamma_{ss}(\text{mNm}^{-1}) = RT\Gamma_s 10^3 \ln(1 - K_s a_s) \quad (4)$$

where $\gamma$ is surface tension, $R$ is gas constant (=8.31 JK$^{-1}$ mol$^{-1}$), $K$ is the equilibrium absorption constant of sulphur, $\Gamma$ is the saturated surface excess concentration, $a_s$ is activity of Sulphur in the metal, and the subscripts "pure" and "ss" refer to the clean metal (zero S + O) and the alloy, respectively. The following procedure was used:

(1) Measurements of surface tensions of $\gamma_{pure}$ were calculated and averaged at the various temperatures using Equation 5:

$$\gamma_{pure}(\text{mNm}^{-1}) = 1840\text{–}0.4(T - 1823) \quad (5)$$

(2) The surface tensions for the 304 and 316 austenitic steels were calculated at temperatures of 1923, 1973 and 2023 K from the data due to Brooks *et al.* [7] given in Fig. 2 and Equations 1–3.

(3) The surface tensions for 430 stainless steel at 1793, 1835 and 1873 K were calculated from the various equations reported by Li *et al.* [10].

(4) The Henrian activity coefficient of S in the steel ($h_S$) was derived for all the steels using the recommended interaction parameters of first and second order [13]. Values varied between 0.58 and 0.79 (Table II) and a mean value of $h_S = 0.68$ was used to calculate $a_S = (h_S)\%S$ (Standard state 1 wt% S in steel).

(5) The surface tension of the alloy, $\gamma_{ss}$was plotted against $\ln a_S$ and the parameter $\Gamma_S$ was determined from the gradient ($d\gamma/d\ln a_S$) according to the Gibbs adsorption equation: $\Gamma_s = -(1/RT) \cdot (d\gamma/d\ln a_s)_T$.

(6) The maximum value of $\Gamma_{max}$ was adopted and substituted into Equation 4 to derive a value of $\ln K_s$ for the higher $S$ concentrations.

(7) Then $\ln K_s$ was plotted as a function of $1/T$ (where $T$ is in $K$) to derive the parameters $K_s$ and $A$ in Equation 6:

$$\ln K_s = \ln k_s + A/T \quad (6)$$

where $k_s$ is a pre-exponential term and $A = \Delta H^{abs}/R$ and $\Delta H^{abs}$ is the enthalpy of adsorption of $S$ by the metal. The results are shown in Equation 7.

TABLE II Henrian activity coefficients for various steels

| Type | Austenitic[a] | Ferritic | Martensitic* |
|---|---|---|---|
| $h_S$ (average) | 0.59–0.72 (0.66) | 0.58–0.73 (0.64) | 0.77–0.79 (0.78) |

[a] Assuming the alloys containing 500 ppm Al, 0–300 ppm S, 30 ppm O, the average values of the other element contents are used.

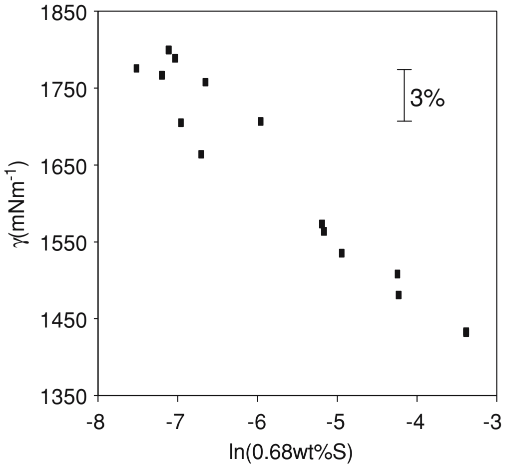


*Figure 4* Surface tension as a function of $\ln a_s$ (ln 0.68 wt%S).

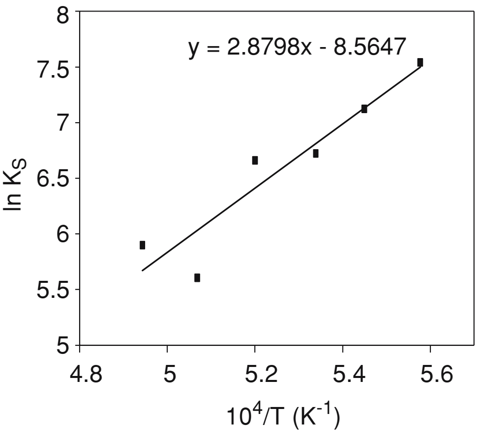


*Figure 5* Logarithm of absorption coefficient of S ($\ln K_s$) as a function of reciprocal temperature ($K^{-1}$).

## 4. Results and discussion

The above analysis of the data yielded the values of $\Gamma_S^{\max}$. The following values were obtained for $\Gamma$: for 304 and 316, $\Gamma = 6.03 \times 10^{-6}$ mol/m$^2$, for 430 $\Gamma = 7.37 \times 10^{-6}$ mol/m$^2$. A mean value of $\Gamma = 6.7 \times 10^6$ mol/m$^2$ was obtained. The plot of $\ln K_s$ as a function of reciprocal temperature (Fig. 5) yielded the equation:

$$\ln K_s = (28798/T) - 8.5647 \tag{7}$$

The above value for $A$ leads to an enthalpy of absorption of $\Delta H^{\text{abs}} = 239$ kJ mol$^{-1}$.

It should be noted that the value of $\Gamma s$ is about half that obtained for $\Gamma s$ for the Fe-S system [14] ($\Gamma s = 14.2 \times 10^{-6}$ mol/m$^2$), which suggests that for most stainless steel compositions, $\Gamma s$ is not at the saturation values.

Using the values for $\Gamma$, $k_s$ and A and Equations 4 and 5, the following relation was derived:

$$\gamma(\text{mNm}^{-1}) = 1840\text{–}0.4(T - 1823) - 0.056T\,\text{Ln} \times \left\{1 + e^{\frac{28798}{T} - 8.5647}(0.68\%\text{S})\right\} \tag{8}$$

Differentiation of this equation gives

$$\frac{d\gamma}{dT}(\text{mNm}^{-1}\text{K}^{-1}) = -0.4 - 0.056\left(\frac{28798(1-B)}{BT} + \ln B\right) \tag{9}$$

Where $B = 1 + e^{(28798/T - 8.5647)}(0.68\text{ wt\%S})$

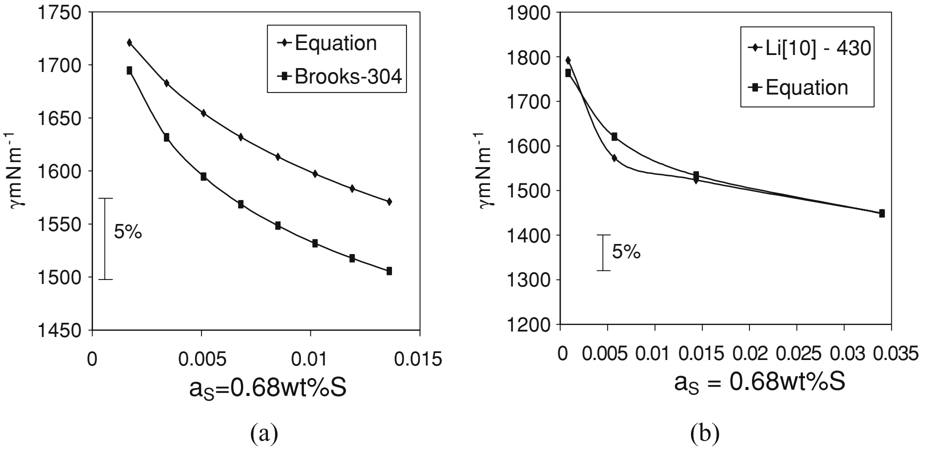
Surface tension values calculated with Equation 8 are plotted against experimental values due to Brooks *et al.* [7] and Li *et al.* [10] in Fig. 6.

The values of $d\gamma/dT$ derived from Equation 9 are plotted against measured values due to Brooks *et al.* [7] and Fig. 7 and with estimated values reported by McNallan and Debroy [15].

### *The effect of Al content and temperature on %O*

In some stainless steels the Al content may be sufficiently low to allow a greater soluble $\underline{O}$ content than the 5 ppm assumed in this study. For steels containing enough S to completely cover the surface (i.e. $\Gamma \approx \Gamma_{\max}$ which occurs around 0.05%$\underline{S}$) the replacement of $\underline{S}$ by $\underline{O}$ in the surface layer would have little effect on the surface tension. However this is not the case when $\Gamma < \Gamma_{\max}$ (i.e. $\underline{S} \ll 0.05\%$) in these cases the enhanced $\underline{O}$ contents would lead to a lower surface tension.

We have also assumed that the soluble $\underline{O}$ is independent of temperature over the range (1773 to 1973 K)



(a) (b)

*Figure 6* Comparison of the calculated surface tensions with measured values (a) for 304 and 316 stainless steels at 1973 K and (b) 430 stainless steels at 1835 K.

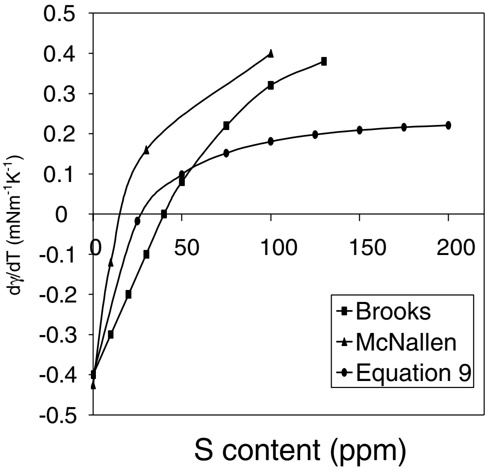


*Figure 7* Calculated temperature coefficients ($d\gamma/dT$) as a function of S content compared with experimental data of Brooks and McNallen at 1925 K.

(i.e. identical to that at 1873 K as shown in Fig. 1). However, the soluble $\underline{O}$% would be expected to increase at higher temperatures. Thus the differences in $\Gamma s$ values obtained from the data due to Brooks *et al.* [7] and by Li *et al.* [10] could possibly be due to the differences in between actual and assumed values of $\underline{O}$%. However, the procedure adopted here of using a mean $\Gamma s$ to calculate $K$ as a function of reciprocal temperature will tend to smooth out these effects on the surface tension. The fact that calculated surface tension values lie within 3% of the measured values supports this view. The experimental measurements are subject to experimental uncertainties of ± 3–5%. However, a more rigorous analysis (which takes into account the temperature dependence of the $\underline{O}$%) may be merited when more accurate surface tension–temperature data become available.

## 5. Conclusions

An equation has been derived to calculate a wide range of stainless steel compositions in terms of the temperature ($\gamma$)

$$\gamma(\text{mNm}^{-1}) = 1840 - 0.4(T - 1823) - 0.056T\text{Ln} \times \left\{1 + e^{\frac{28798}{T} - 8.5647}(0.68\%S)\right\}$$

An equation was also obtained for the temperature dependence ($d\gamma/dT$) of the alloy.

$$\frac{d\gamma}{dT}(\text{mNm}^{-1}\text{K}^{-1}) = -0.4 - 0.056\left(\frac{28798(1-B)}{BT} + \ln B\right)$$

where $B = 1 + e^{(28798/\text{T}-8.5647)}$ (0.68 wt%S).

The surface tensions calculated with the equation are within ±3% of the experimental values and the calculated values of ($d\gamma$/dT) are in good agreement of the measured values.

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