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A model to calculate surface tension of commercial alloys

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A model has been developed for the calculation of the surface tension (γ) and its temperature dependence ($d\gamma/dT$) for commercial alloys (steels and nickel-based superalloys) from (i) the chemical composition and (ii) values of the surface tension and molar volume of the various elemental components. The model was found to give values which were within 6% of the measured values for steels and the ($d\gamma/dT$) results were similar to measured values. Although there are more difficult problems to be overcome with Ni-superalloys, the model predictions appear to be within 5% of the measured values.

1. Introduction

Many high-temperature industrial processes are affected by Marangoni flows or interfacial phenomena. Marangoni flows arise in response to a surface tension gradient and the flow is always in the direction of low to high surface tension. In some of these processes the fluid flow is dominated by Marangoni flows (e.g. in TIG welding [1] and growth of single crystals by Floating zone [2] and Czochralski processes [3]). Thus when developing models of the combined fluid flow and heat transfer in a process it is important to take these flows into account. This requires a knowledge of the surface tension (γ) and the temperature coefficient ($d\gamma/dT$). Both the surface tension and temperature coefficients ($d\gamma/dT$) of metals are very sensitive to the concentrations (at ppm levels) of surface-active elements, such as S and O. Furthermore, the concentrations of *soluble* O and S (denoted here as $\underline{O}$ and $\underline{S}$) are affected by the presence of other elements such as Al in the case of O and Ca and Ce in the case of S (Fig. 1). Although there are materials specifications for many commercial alloys there are always small compositional differences especially in those elements present in ppm levels, such as O, S and Ca. Consequently, when measurements of surface tensions are made on metals and alloys, the values pertain to the sample in question but not to other batches of the alloy with different $\underline{O}$ and $\underline{S}$ contents. For this reason it is important to develop a model which will allow calculation of the surface tension and ($d\gamma/dT$) of alloys with other O and S contents. Consequently, the objective of this work was to develop a model which would be applicable to multi-component alloys.

The model was first developed for steels because the chemical activities of the binary systems involving the major components in steels (Fe, Cr, Ni, Mn) are close to ideal and have very similar surface tensions. The model was then extended to other alloys (such as Ni-based superalloys) which contain significant concentrations of elements (e.g. Al) whose chemical activities show large departures from ideality.

Several models have been reported for the calculation of surface tensions of binary and ternary alloys from a knowledge of (i) composition (ii) molar volumes and (iii) surface tensions of the component metals [5–7]. McNallan and Debroy [8] calculated the surface tensions of Fe-Cr-S alloys for compositions covering the range of stainless steels. No models have been proposed for calculating the surface tensions of multi-component alloys.

The model presented here for the estimation of surface tensions of steels contains 3 steps:

1. Calculation of the overall surface tension (γ) and ($d\gamma/dT$) of metallic components using the method due to Hajra *et al.* [5] utilising surface tensions and the surface areas of the pure metal components.
2. Calculation of the *soluble* $\underline{O}$% and $\underline{S}$% contents (Fig. 1 [4])
3. Calculation of the effect of $\underline{O}$% and $\underline{S}$% on both (γ) and ($d\gamma/dT$) making use of Equation 1 and relations due to Belton [9] for the effect of surface active components, e.g. S:

$$\gamma_{\text{pure}} - \gamma_{\text{alloy}} = RT\Gamma_s \ln(1 - K_s a_s) \qquad (1)$$

where R = Gas constant, T = temperature (K); Γ_s = Saturated surface excess concentration; K = Absorption coefficient and the subscripts "pure" and "alloy"

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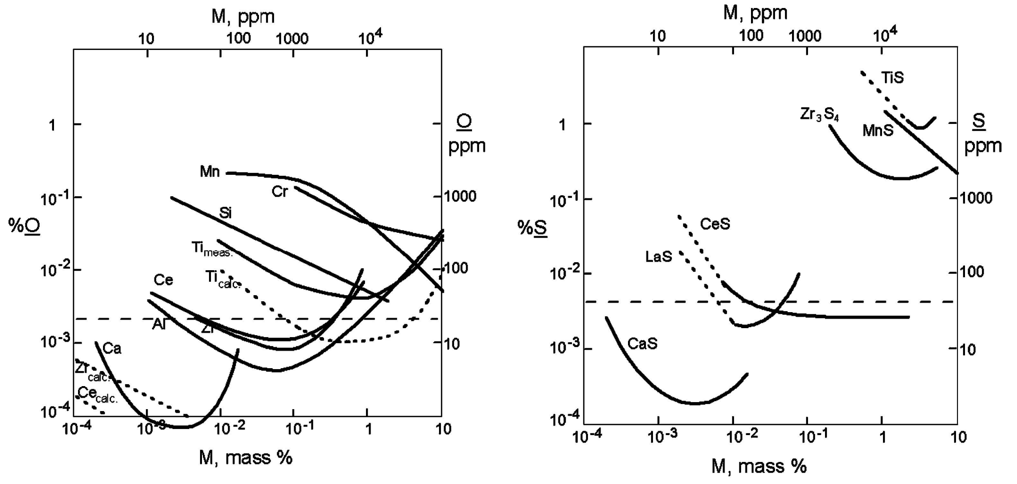

(a) (b)

Figure 1 The effect of different alloying additions (M) on (a) the soluble $\underline{O}$ % content in the Fe-M-O system and (b) the soluble $\underline{S}$% content in the Fe-M-S system [4].

refer to metal with O and S contents of zero % and actual contents in alloy, respectively.

It should be noted that the experimental uncertainty associated with surface tension measurements on metallic elements is at least ±2–3% and is probably higher where there is some uncertainty in the concentrations of soluble $\underline{O}$ and $\underline{S}$. The experimental uncertainties for surface tensions of commercial materials are higher than those of pure metals. Thus differences between calculated and measured values of ±5% could be considered to be very satisfactory.

2. Data used in model

The values of the surface tension, molar volume and melting points of the elements used in the calculations are given in Table I. The surface tension values were obtained from both the review due to Keene [10] and from recent measurements.

Typical compositions of the alloys used in this study are given in Table II.

3. Phase 1 model

The Phase 1 model was developed to calculate the surface tensions of ferritic and stainless steels making use of the following assumptions:

1. Solution of various elements (e.g. Cr, Ni etc.) is ideal.
2. Those elements which are non-ideal (e.g. Al) are present in such low concentrations that they do not affect surface tension significantly.

TABLE I Values of surface tension and molar volume for elements used in the calculation where $\gamma = \gamma^m - A(T - T^m)$ and $V = V^m + B(T - T^m)$ and m = melting point

Element	γ^m	A	T^m(K)	V^m	10^4B	T^m(K)
Fe	1909	−0.52	1803	7.94	1.19	1803
Cr	1700			8.27		
Mn	1219	−0.35	1518	9.54	1.27	1518
Mo	2250			10.26		
Ni	1834	−0.376	1728	7.43	1.42	1728
Si	859	−0.145	1683	11.1	1.45	1683
Ti	1650			11.6		
V	1950			9.50		
Al	890	−0.182	933	11.3	1.14	933
Ca	360	−0.10	1123	29.5	1.62	1123

3.1. Procedure for the calculation of surface tension of metallic components of alloy

1. The mole fractions of each component were calculated
2. The surface tensions (γ_T^i) for each element at the required temperature were calculated using the formula $\gamma_T^i = \{\gamma_i^{mp} + A(T - T^{mp})\}$ and the values given in Table I, where the superscript mp refers to the melting point.
3. The molar volumes (V_i) at the required temperature were calculated for each element using $V_i = V^{mp} + B(T - T^{mp})$ using the values given into Table I.
4. The surface area (s_i) for each element was calculated using $s_i = (0.921\ V_i^{2/3}) \times 10^4$
5. The surface tension of metal (γ_T) was then calculated by solving the following relation; $1 = \Sigma x_i \exp\{(\gamma_T - \gamma_T^i)s_i/R'T\}$ (see footnote[1])
6. Soluble %$\underline{O}$ and %$\underline{S}$ calculated in Step 2 are converted into activities, a_s and a_o (reference state-1 wt%)
7. Values of K_s and K_o, (adsorption coefficients for S and O) at various temperatures [6] were derived using

$$\ln K_s = (-5.75 + 20 \times 10^3/8.31T) \quad (3)$$

$$\ln K_o = (-1.85 + 13.2 \times 10^3/8.31T) \quad (4)$$

8. Surface tension depressions, L and M, due to $\underline{S}$%, and $\underline{O}$% in alloy were calculated.

$$L = R'T\Gamma_o\{(1 + K_oa_o + K_sa_s)/(1 + K_sa_s)\} \quad (5)$$

$$M = R'T\Gamma_s\{(1 + K_oa_o + K_sa_s/(1 + K_oa_o)\} \quad (6)$$

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[1] Since the surface tensions and molar volumes of most of the component elements are very similar, the surface tension can be calculated from $\gamma_T = x_1\gamma_1 + x_2\gamma_2 + x_3\gamma_3 + \cdots$ without much loss in accuracy.

TABLE II Typical compositions of alloys studied in this investigation

Alloy	% C	% Fe	% Ni	% Cr	% Mo	% Mn	% Si	%Nb /Ta	% Re	% Ti	% W	% Co	O (ppm)	S (ppm)
C/Mn	0.70	Bal	–	–	–	1.1	0.35						8	200
304	0.04	Bal	9.3	19	0	1	0.5							
316	0.04	Bal	12	17	2.5	1	0.5							
430	0.06	Bal	0	17	0	0.5	0.5							
IN 718	0.08	16.7	Bal	19	3.1	0.4	0.4	5.2	–	0.9		1		
CMS X4	0.006	0.2	Bal	6.5	0.6	–	0.04	−Ta 6.5	3	1	6.4	10	2	2

where Γ_o and Γ_s are values of surface concentration of O and S at full coverage.

9. The total surface tension depression, $\Delta\gamma$, was calculated by

$$\Delta\gamma = L + M \tag{7}$$

3.2. Application of Phase 1 model to steels

Most steels contain at least 50 ppm Al and thus the soluble $\underline{O}$ is low (4 ppm) (see Fe-Al-O in Fig. 1a) whereas the *soluble* $\underline{S}$ is assumed to be similar to the *total* S.

3.2.1. C/Mn ferritic steel

Surface tension values were calculated for the steel composition listed in Table II. The results shown in Fig. 2 indicate that the measured results due to Seetharaman [11] lie about 10 and 6% higher than the calculated values. A positive temperature dependence ($d\gamma/dT$) might be expected for a sample with (4 ppm $\underline{O}$ and 200 ppm $\underline{S}$).

3.2.2. Austenitic stainless steels

Surface tensions have been reported by Brooks and Mills [12] for 304 and 316 stainless steels. Values have been calculated for 304 and 316 stainless steels and are compared with measured values in Fig. 3 and values of ($d\gamma/dT$) are given in Fig. 4. It can be seen from Figs 3 and 4 that:

1. The calculated values for the surface tension at 1973 K are 3–5% higher than experimental values reported by Brooks and Mills [12].

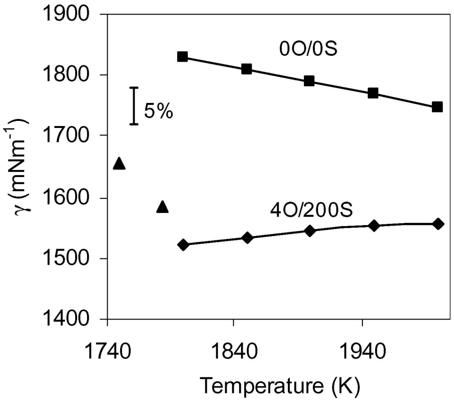


Figure 2 Comparison of calculated surface tension values for C/Mn steel containing (0 ppm O + 0 ppm S) and (4 ppm O + 200 ppm S) with measured values; ▲.

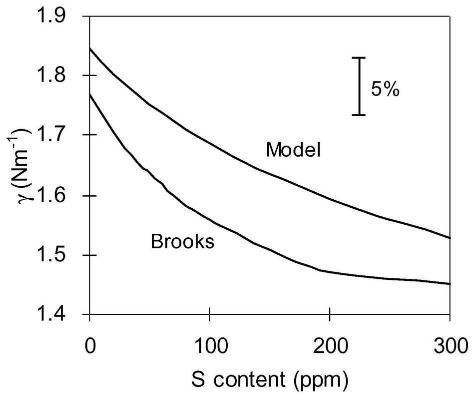


Figure 3 Comparison of calculated and measured [12] values of surface tension of 304/316 stainless steels at 1973 K.

2. That ($d\gamma/dT$) from the alloy changes from negative to positive values and exhibits similar behavior to that of the Fe-O and Fe-S systems with respect to temperature and *S* content.

3. The 'crossover' point (where ($d\gamma/dT$) $= 0$ i.e. point where sign changes) at 1973 K occurs at a S content around 80 ppm compared with a measured value of 40 ppm and a calculated value of 15 ppm due to McNallan and Debroy [8].

4. The S content at the 'crossover' point increased with increasing temperature.

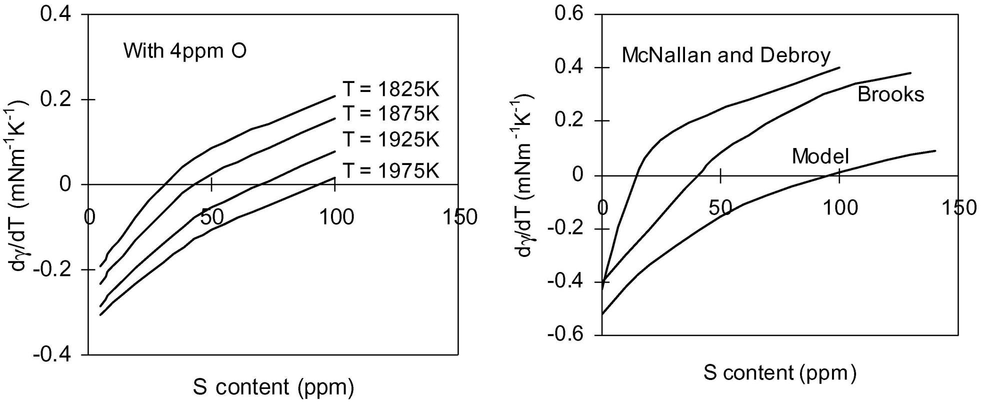
Surface tension values were estimated using the model for a stainless steel containing 25.6%Cr, 6.5%Ni, 4%Mo, 0.5%Mn and a S content of <5 ppm. The calculated surface tension value (1830 mNm^{-1}) was in good agreement (ca. 2%) with the measured value of 1790 mNm^{-1} at 1866 K due to Seetharaman *et al.* [11].

3.2.3. Ferritic stainless steels

Li *et al.* [13] have reported surface tension data for ten ferritic (430) stainless steels (Fig. 5). It can be seen from this figure that the calculated values are for the most part within 2% of the measured values and always lie within 6% of the measured values.

4. Phase 2 model

It can be seen above that the Phase 1 model was capable of calculating values of the surface tensions of both C/Mn and stainless steels to within ±5% of the measured values. However, there are problems when trying to calculate the surface tensions of Ni- base superalloys:



(a) (b)

Figure 4 Effect of S content on ($d\gamma/dT$) (a) showing the effect of temperature and (b) comparing model predictions with experimental data [12] and estimated values due to McNallen [8].

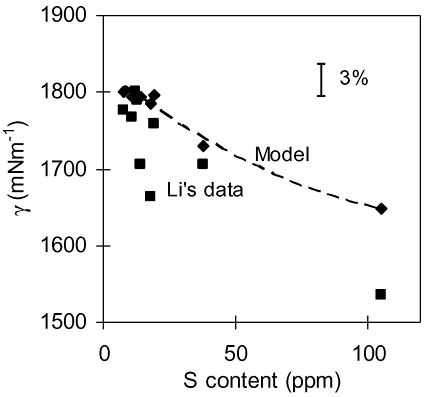


Figure 5 Comparison of calculated and measured surface tensions of ferrite stainless steel 430 as a function of S content at 1823 K, ■ experimental [13]; ♦ calculated.

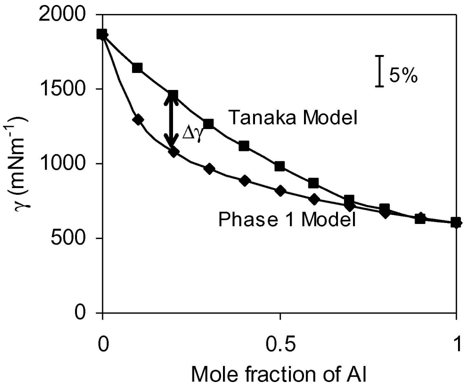


Figure 6 Comparison of the surface tension values for the Fe-Al system calculated with Phase 1 and Tanaka [7] models.

1. Some Ni superalloys contain appreciable levels of Al and the activity of Al (a_{Al}) in Ni-Al show a strong negative departure from ideality, leading to a higher surface tension than that calculated with the Phase 1 model (the low chemical activity, a_{Al} means that there is less Al at the surface than that where the element exhibits ideal behaviour).

2. The *soluble* $\underline{\mathrm{O}}$% or (a_{o}) levels for the Fe-Al-O system (as calculated from interaction coefficients) tend to increase with increasing Al contents above 0.1% Al (Fig. 1) whereas in contrast, Regular solution calculations [14] carried out recently show no increase in $\underline{\mathrm{O}}$% with increasing Al content above 0.1%.

3. Ni-based superalloys contain a large number of elements in significant concentrations and it is difficult to apply Equation 1 to multi-component systems.

4. W, Ta, Re have high melting temperatures and would be solid at temperature of interest and Al is well above its melting point; so in the Phase 2 model the melting temperatures of these elements have been taken as those of the host element, Ni.

4.1. Outline of Phase 2 model

The above problems have been addressed in the following manner.

1. The effect of non-ideality i.e. (a_{Al}) of the Ni-Al system was taken into account by calculating the difference in surface tension, $\Delta\gamma$, between the values of γ calculated, obtained with the Phase 1 model for the Fe-Al system and that calculated using Tanaka's model [7] (which takes non-ideality into account using the excess free energy) as can be seen in Fig. 6.

2. The adopted procedure assumed that $\Delta\gamma$ for the Ni-Al system was identical to that for Fe-Al shown in Fig. 6 (Subsequent calculations for Ni-Al using a model [15] similar to that reported by Tanaka [7] and thermodynamic values from MTDATA [16] resulted in values of $\Delta\gamma$ identical to those shown in Fig. 6.

3. The system was treated as a pseudo-ternary, in which metallic components were divided into different groups ('Ni', 'Nb' and Al) and mean values of γ and V for 'Ni', 'Nb' were calculated as a weighted mean based on the mole fractions (x), e.g. $\gamma_{\mathrm{T}}(\text{'Ni'}) = (\times\gamma)_{\mathrm{Ni}} + (x\gamma)_{\mathrm{Fe}} + (x\gamma)_{\mathrm{Cr}}$; the following steps were taken

(i) The effect of Fe, Cr, Co on γ (Ni) was determined to obtain γ ('Ni')
(ii) The effect of Nb, Re, Mo, W on γ ('Ni') was then determined to obtain γ ('Ni' + 'Nb')
(iii) The effect of Al on γ ('Ni' + 'Nb') was determined to give γ ('Ni' + 'Nb' + Al) i.e. the surface tension of the ideal γ ('Ni' + 'Nb') was modified by adding the appropriate $\Delta\gamma$ value for the mole fraction Al

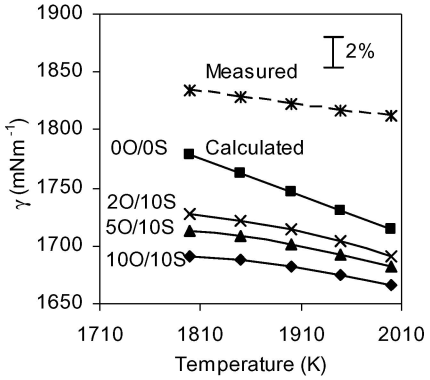


Figure 7 Comparison of the calculated and measured [17] surface tension of IN718 system with various S̲ and O̲ contents.

4. It was also assumed that *soluble* O% values for Ni-Al were identical to those for Fe-Al (Fig. 1) and that Regular Solution results apply (i.e. soluble O̲% of 4–5 ppm and there is no increase in O̲% with increasing Al content).

5. It has been assumed that for the calculation of γ_i, V_i and s_i at a specific temperature that melting temperatures of W, Ta, and Re and Al were identical to that of Ni.

4.2. Application to Ni-based superalloys

4.2.1. Ni-based superalloy IN718

The performance of the model was first checked by comparing calculated surface tension values with experimental results reported by Brooks *et al.* [17] for Ni-based alloy IN718 which contains 0.5%Al. The calculated values were about 60–100 mNm^{-1} (or 5% lower) than the measured values.

4.2.2. CMSX 4

The calculated results for CMSX 4 are shown in Figs 8 and 9. It can be seen from Fig. 8 that if Al is considered ideal it appears to cause a significant decrease in surface tension but corrections for the strong negative departures of a_{Al} from ideality in the Ni-Al system resulted in a large increase in γ, thereby cancelling out most of the decrease in surface tension due to the Al. The effect of temperature and (O̲ + S̲) content on the surface tension of CMSX4 is shown in Fig. 9.

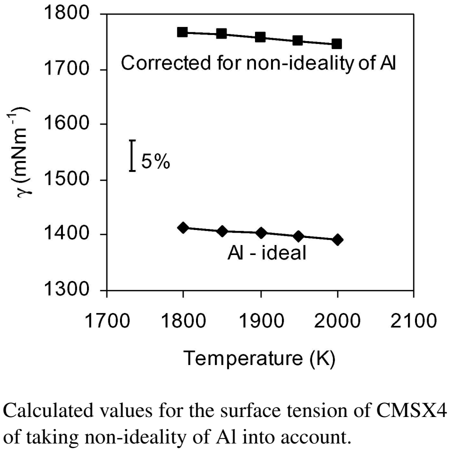


Figure 8 Calculated values for the surface tension of CMSX4 showing the effect of taking non-ideality of Al into account.

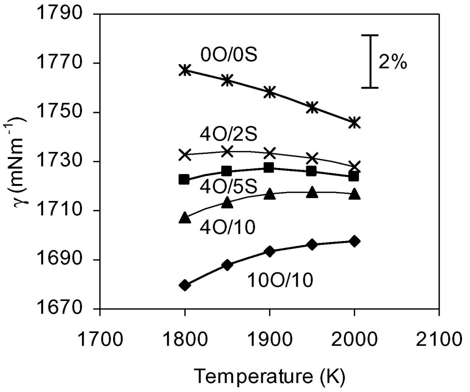


Figure 9 Calculated values of surface tension of CMSX4 as a function of temperature showing the effects of different levels of soluble O̲ and S̲.

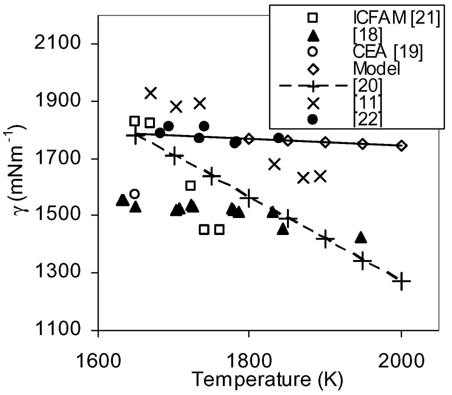


Figure 10 Comparison of measured surface tension as a function of temperature of CMSX 4 [11, 18–22].

Some uncertainty in the calculations may arise from the solution of the equation $(1 = \Sigma x_i \exp\{(\gamma_T - \gamma_T^i)\, s_i/RT\})$ to obtain γ_T if the solution lies in a "flat-bottomed valley". In these cases values for the "pure alloy" can be obtained using the method outlined in Footnote 1.

There have been several recent experimental studies of the surface tension for CMSX4 [11, 18–22]. The results are shown in Fig. 10 and it is apparent that there is considerable scatter in the results. As can be seen from Fig. 10 the values calculated using the Phase 2 model support the higher values but have a much smaller temperature dependence than those recorded in the experimental studies. Two possible explanations have been suggested for the scatter in Fig. 10.

1. Vaporisation of Al during the measurements
2. A significant change in the soluble O content of the alloy at higher temperatures.

It has been suggested that one possible reason for the scattered data could lie in the evaporation of Al from the free surface. In order to examine this possibility the surface tensions of alloys containing 5.6 and 3% Al were calculated. It was found that the evaporation of Al resulted only in a slight increase (8 mNm^{-1} or 0.5%) in surface tension. Thus the scatter in the measured values is not due to Al evaporation.

It is our opinion that the large experimental values for the temperature dependence ($d\gamma/dT$) are due to increases in *soluble* $\underline{O}$ content with increasing temperature and this causes a concomitant decrease in the surface tension and hence a more negative value for $(d\gamma/dT)$.

It should also be pointed out that there is a difference in the soluble O content at Al contents $>1\%$ calculated from interaction coefficients and those calculated from Regular solution. We have assumed Regular solution but it is possible that the soluble O contents are higher than the values we have assumed; this would leave to lower surface tensions.

5. Conclusions

1. The calculated surface tensions were mostly within 5% of the measured values for most alloys.
2. The calculated values for $(d\gamma/dT)$ for different O and S contents are very similar to the measured values which indicates that the model would be very useful for deriving the surface tension of different batches of alloys with different O and S contents.
3. The model is useful for predicting the effects of differing composition on the surface tension (e.g. the effect of Al vaporisation).
4. Further work is needed to calculate both the *soluble* $\underline{O}$% for Ni-Al-O system and the current differences between $\underline{O}$% values calculated from interaction coefficients and those from Regular solution.

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