

# Surface Tension of Binary Metal—Surface Active Solute Systems under Conditions Relevant to Welding Metallurgy

P. SAHOO, T. DEBROY, and M. J. McNALLAN

Since the fluid flow, heat transfer, and the resulting weld properties are significantly affected by interfacial tension driven flow, the variation of interfacial tension in dilute binary solutions is studied as a function of both composition and temperature. Entropy and enthalpy of adsorption of surface active components such as oxygen, sulfur, selenium, and tellurium in Fe-O, Fe-S, Fe-Se, Cu-O, Cu-S, Cu-Se, Cu-Te, Ag-O, and Sn-Te systems were calculated from the analysis of the published data on interfacial tension of these systems. For these calculations, a formalism based on the combination of Gibbs and Langmuir adsorption isotherms was used. Interfacial tensions in Cr-O, Co-S, and Ni-S systems, where the data are scarce, were predicted by using certain approximations. The computed values were found to be in reasonable agreement with the data available in the literature. Temperature coefficients of interfacial tensions were calculated for several binary systems. It was demonstrated that in dilute solutions, the temperature coefficient of interfacial tension is strongly influenced by the heat of adsorption which, in turn, is influenced by the difference in electronegativity between the solute and solvent ions.

## I. INTRODUCTION

RECENT studies have demonstrated that, in many cases, the fluid flow, heat transfer, and the resulting weld shape, size, and properties are significantly influenced by the Marangoni convection.<sup>[1,2]</sup> Presence of a surface active element significantly alters the surface tension of the solvent. Furthermore, these elements often change the temperature dependence of surface tension ( $d\gamma/dT$ ) from a negative value for pure solvents to a positive value for binary systems. This change in the sign of  $d\gamma/dT$  has a significant implication in several practical systems. Of particular practical significance is the reversal in the direction of circulation in the weld pool which occurs in steels in the presence of small amounts of surface active impurities. The flow reversal results in deeper weld penetration at particular welding speeds and power levels during welding<sup>[3]</sup> and it is believed that steels containing small amounts of surface active elements may be more easily fabricated than clean steels which contain very low levels of impurities.

While this effect has been identified, the details of the interactions between temperature, impurity levels, and surface tension are not well understood and optimum impurity levels for different welding processes cannot be specified. Most of the impurity elements which affect surface tension driven flow have deleterious effects on the mechanical properties of steel. If such elements were to be present in steels for improved weldability, it would be important for the steel to contain the lowest level of the surface active element necessary to produce improved weld penetration.

The surface tension driven flow in weld pools is influenced by the temperature dependence of the surface tension. The fluid flow within the weld pool is strongly affected by the steep temperature gradients in the pool and by the tem-

perature dependence of the surface tension of the metal. In pure metals, the surface tension decreases with increasing temperature. In a dilute alloy containing a single surface active component, the surface tension is affected by the segregation of the surface active component to the surface and may increase or decrease with temperature depending on the thermodynamics of the segregation process. In this paper, we have reviewed the thermodynamics of adsorption of surface active elements on metal surfaces with the intention of defining the relationships between surface tension, temperature, and composition under conditions relevant to welding metallurgy.

## II. BACKGROUND

The temperature coefficient of surface tension of pure metals and their alloys can be estimated from a knowledge of factors such as melting point, molar volume, atomic number, and heat of vaporization. However, this approach cannot be easily extended to systems with a surface active component because of the radical changes in the nature of the surface layer when these surface active elements are present. One of the first major publications dealing with the effect of surface active agents on the surface tension of solutions was given by Szyszkowski<sup>[4]</sup> in 1908. He derived the following empirical relation:

$$\frac{\gamma^\circ - \gamma}{\gamma} = b \ln \left[ \frac{C_2}{C} + 1 \right] \quad [1]$$

where  $\gamma^\circ$  is the surface tension of the pure solvent,  $\gamma$  is the surface tension of the solution,  $C_2$  is the molality of the solution, and  $b$  and  $C$  are constants. Bernard and Lupis<sup>[5]</sup> developed a statistical model on the basis of formation of a compound  $A_{n-1}B$  at the surface when the solute element,  $B$ , provides maximum surface coverage. The model takes into account the net attractive forces between the adsorbed solute atoms. Application of their formalism to the Fe-O and Ag-O systems produced a semi-empirical correlation between surface activity and solute concentration. Although the cor-

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relation is useful for predicting the depression of surface tension with concentration, prediction of temperature coefficient of interfacial tension using the current form of the correlation is not straightforward.

Belton<sup>[6]</sup> has used a combination of Gibbs and Langmuir adsorption isotherms to develop a formalism which describes the interfacial tension of a liquid metal in the presence of a surface active element. The relationship is given by:

$$\gamma^{\circ} - \gamma = RT\Gamma_s \ln[1 + Ka_i] \quad [2]$$

where  $\Gamma_s$  is the surface excess at saturation,  $K$  is the adsorption coefficient, and  $a_i$  is the activity of species  $i$  in solution.

Although Eq. [2] is derived to express interfacial tension as a function of both temperature and composition from first principles, the variation of the adsorption coefficient  $K$  with respect to temperature is not explicitly defined. This, however, can be readily achieved by considering the following reaction:



in which the dissolved solute component  $i$  segregates to a surface site  $v^s$  in order to form an occupied site  $i^s$ . For single site occupancy the equilibrium constant  $K$  for reaction [3] is given by:

$$K = e^{-(\Delta G^{\circ}/RT)} = \frac{\theta_i}{a_i(1 - \theta_i)} \quad [4]$$

where  $\theta_i = \Gamma_i/\Gamma_s$  is the fractional surface coverage of  $i$  and  $a_i$  is the thermodynamic activity of component  $i$  in the solution. The equilibrium constant can be broken up into its two components and is given by:

$$K = e^{(\Delta S^{\circ}/R)} e^{-(\Delta H^{\circ}/RT)} = k_1 e^{-(\Delta H^{\circ}/RT)} \quad [5]$$

where  $k_1$  is a constant which is related to the entropy of segregation, and  $\Delta H^{\circ}$  is the standard heat of adsorption. The constants  $k_1$  and  $\Delta H^{\circ}$  are assumed to be independent of temperature and can be obtained for any combination of

solvent and surface active solute by measuring surface tension as a function of  $a_i$  at least at two temperatures. Combining this with the temperature dependence of the surface tension for the pure metal, the following relation is obtained for the surface tension of metal-solute ( $i$ ) alloys as a function of both temperature,  $T$ , and activity,  $a_i$ .

$$\gamma = \gamma_m^{\circ} - A(T - T_m) - RT\Gamma_s \ln[1 + k_1 a_i e^{-(\Delta H^{\circ}/RT)}] \quad [6]$$

In Eq. [6],  $\gamma_m^{\circ}$  is the surface tension of pure metal at the melting point,  $A$  is the negative of  $d\gamma/dT$  for pure metal, and  $T_m$  is the melting point of the material. For several metals such as Cu, Zn, and Pb and for alkali metals it is known that  $A$  is a constant for temperatures much above their melting points. In Eq. [6] and in subsequent discussions, it is assumed that  $A$  is a constant.

### III. RESULTS AND DISCUSSION

#### A. Estimation of Enthalpy ( $\Delta H^{\circ}$ ) and Entropy Factor ( $k_1$ )

Examination of Eq. [6] reveals that four factors ( $A$ ,  $\Gamma_s$ ,  $k_1$ , and  $\Delta H^{\circ}$ ) must be known before the surface tension of the binary solution can be calculated.  $A$ , which is the negative of the temperature coefficient of surface tension of a pure metal, can be determined from the surface tension values at two or more temperatures. The constant  $A$  can also be estimated by means of expressions based on Eotvos' Law, and the procedures are discussed by Allen.<sup>[7]</sup> The surface excess of the solute species at saturation,  $\Gamma_s$ , can be determined by applying Gibbs isotherm to a surface tension vs activity plot. In the absence of experimental data,  $\Gamma_s$  may be estimated from a knowledge of the surface structure. Table I shows that such an estimation indeed yields fairly satisfactory values,<sup>[8]</sup> especially when one considers the uncertainty in the experimental data. In fact, both  $A$  and  $\Gamma_s$  have been extensively studied for most systems and are either readily available or can be calculated easily.<sup>[8-12]</sup> The means of estimating the two other factors,  $\Delta H^{\circ}$  and  $k_1$ , are now discussed. At a given temperature the equilibrium constant

Table I. Area Requirements at Saturation<sup>[8]</sup>

System 1-2	T (K)	Area Occupied by a Single Solute Atom at the Surface ( $\text{\AA}^2/\text{Atom}$ , $1 \text{\AA} = 10^{-10} \text{ m}$ )			Ionic Radius ( $\text{\AA}$ )		Ionic Charge	
		Experimental	Calculated <sup>a</sup>	Calculated <sup>b</sup>	$r^-$	$r^+$	$Z^-$	$Z^+$
Fe-O	1823	10.3	6.0	8 (111)	1.33	0.83	2	2
Fe-S	1823	15.1	10.5	12 (010)	1.74	0.83	2	2
Fe-Se	1823	14.7	13	13 (010)	1.91	0.83	2	2
Fe-Te	1823	15.0	14.6		2.11	0.83	2	2
Cu-O	1273	29	6.0	18 (100)	1.32	0.96	2	1
				30 (111)				
Cu-S	1393	14.5	10.5	14.5 (100)	1.74	0.96	2	1
				16.8 (111)				
Cu-Se	1423	11.9	13		1.91	0.96	2	1
Cu-Te	1423	13.8	14.6		2.11	0.96	2	1
Ag-O	1253	34	6.0	23 (100)	1.32	1.13	2	1
				38 (111)				

<sup>a</sup>On the basis of monolayer of close-packed solute anions.

<sup>b</sup>On the basis of the solid compound.

for the adsorption reaction (reaction [3]) otherwise referred to as the adsorption coefficient,  $K$ , is determined by fitting experimental surface tension vs composition data to Eq. [2] in which all the parameters except  $K$  are known. If the natural logarithm of the equilibrium constant  $K$  is plotted as a function of  $1/T$ , the values of  $\Delta H^\circ$  and  $k_1$  can be determined from the slope and the intercept of the straight line, respectively.

Since the evaluation of  $K$  requires a series of surface tension measurements on high purity liquid metals at various concentrations of surface active impurities at two, or preferably more temperatures, such data are available for very few systems. The Fe-S system has been one of the most thoroughly studied and the surface tension data for this system is used to calculate  $K$  as a function of temperature. The calculated values of  $K$  are presented as a function of  $1/T$  in Figure 1(a). From this plot the values of the heat of adsorption,  $\Delta H^\circ$  and the entropy factor,  $k_1$ , are determined to be  $-1.66 \times 10^5$  KJ/Kg mole and 0.00318, respectively. The resulting expression for the interfacial tension values of Fe-S alloys as a function of both temperature and composition is given by:

$$\gamma = 1.943 - 4.3 \times 10^{-4}(T - 1809) - RT \times 1.3 \times 10^{-8} \ln[1 + 0.00318a_{\text{S}}e^{[(1.66 \times 10^5)/RT]}] \text{N/m} \quad [7]$$

In order to demonstrate the validity of the above equation, the predictions from Eq. [7] are compared with the experi-

mental values reported by Keene *et al.*<sup>[20]</sup> for the pseudo-binary Fe-S system in Figure 1(b). It may be observed that a fairly good agreement is achieved between the experimental data and the computed values. Table II summarizes the results of similar calculations for various other systems studied and the data sources. In Figures 2 to 4 the predicted interfacial tension values are presented as a function of solute concentration for the Fe-O, Fe-Se, Cu-O, Cu-S, Cu-Se, and Cu-Te systems, respectively. The predicted curves are calculated on the basis of Eq. [6], and the values used for the various systems are summarized in Tables II and III. It can be observed from Figures 2 to 4 that in all cases good correlations are obtained between the predicted and the experimental surface tension values. The good agreements between the experimental and the computed values demonstrate the usefulness of Eq. [6] in predicting the variation of surface tension as a function of composition and temperature.

Unlike the heat of solution data for various systems, the heats of adsorption data are not generally available in the literature. From the previous work, it is known that the heat of adsorption depends on diverse factors such as the difference in electronegativity of the ions, the size difference, type of bonding and the degree of attraction between the ions, the structure of the surface layer, and other parameters of inter-

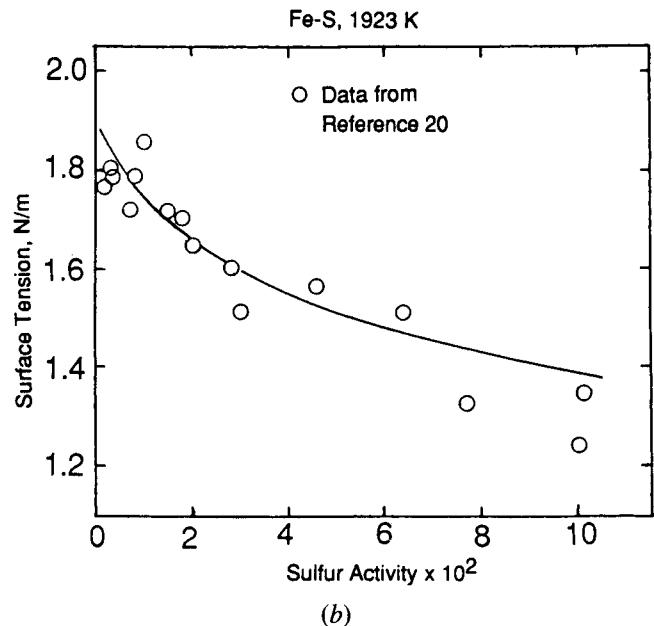
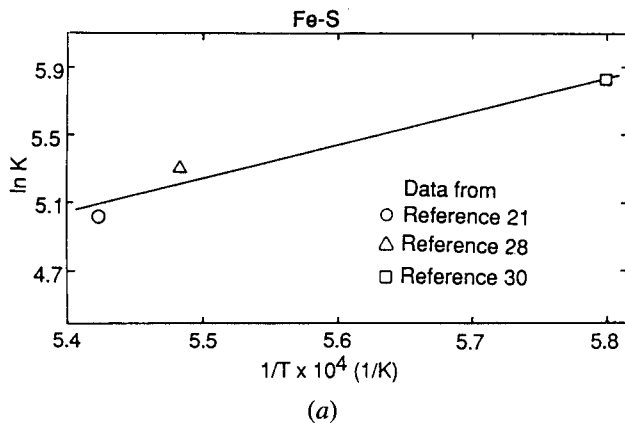


Fig. 1—(a) Variation of equilibrium constant with temperature for the Fe-S system. (b) Depression of surface tension of iron by sulfur. The solid line represents results calculated using Eq. [7]. The data points are taken from Ref. 20.

Table II. Calculated Entropy and Enthalpy Factors

System	$k_1$	$-\Delta H^\circ$ , KJ/Kg Mole	References for Raw Data	Activity Calculations
Fe-O	$1.38 \times 10^{-2}$	$146.3 \times 10^3$	17 to 22, 31	$a_{\text{O}} = \text{wt pct } \bar{\text{O}}$
Fe-S	$3.18 \times 10^{-3}$	$166.2 \times 10^3$	21, 28, 30	$a_{\text{S}} = \text{wt pct } \bar{\text{S}}$
Fe-Se	$8.57 \times 10^{-1}$	$109.8 \times 10^3$	23, 31	$a_{\text{Se}} = \text{wt pct } \bar{\text{Se}}$
Cu-O	$3.29 \times 10^{-1}$	$172.5 \times 10^3$	24 to 26	$a_{\text{O}} = X_{\text{O}} \times \text{activity coefficient}$
Cu-S	$7.94 \times 10^{-5}$	$166.6 \times 10^3$	26, 32	$a_{\text{S}} = \text{at. pct } \bar{\text{S}}$
Cu-Se	$1.45 \times 10^{-3}$	$125.2 \times 10^3$	27	$a_{\text{Se}} = \text{wt pct } \bar{\text{Se}}$
Cu-Te	$1.02 \times 10^{-3}$	$128.9 \times 10^3$	27	$a_{\text{Te}} = \text{wt pct } \bar{\text{Te}}$
Ag-O	—	$142.3 \times 10^3$	10	$a_{\text{O}} = X_{\text{O}} \times \text{activity coefficient}$
Sn-Te	$1.68 \times 10^{-2}$	$37.8 \times 10^3$	28	$a_{\text{Te}} = \text{wt pct } \bar{\text{Te}}$

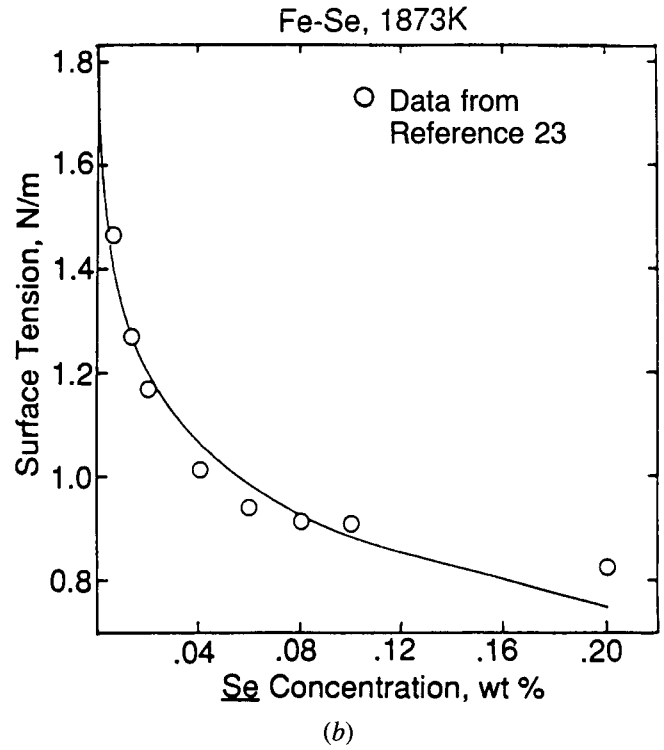
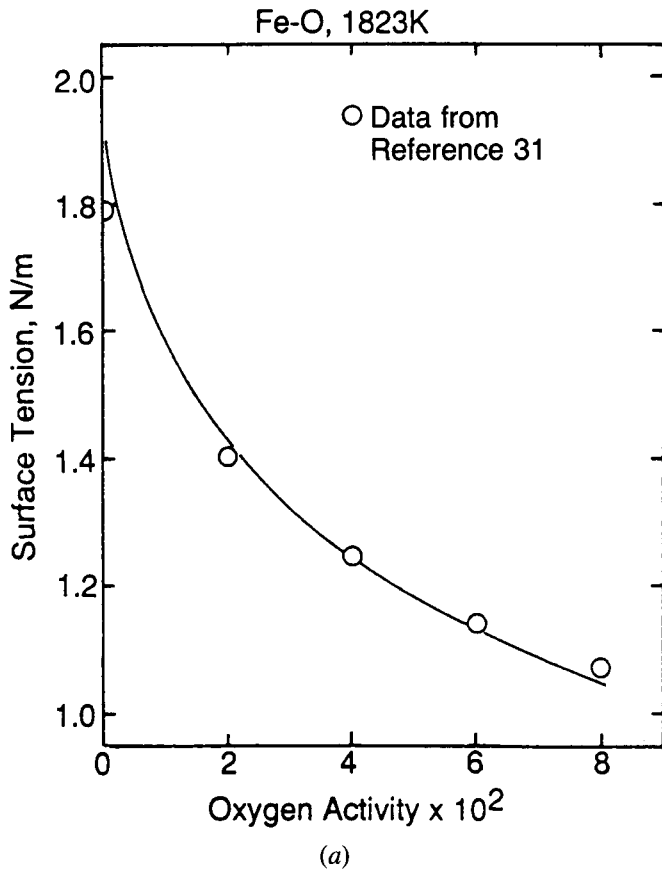


Fig. 2—Depression of surface tension of iron by (a) oxygen and (b) selenium. The solid lines represent results calculated using Eq. [6]. The data points are taken from Refs. 31 and 23 for Fe-O and Fe-Se systems, respectively.

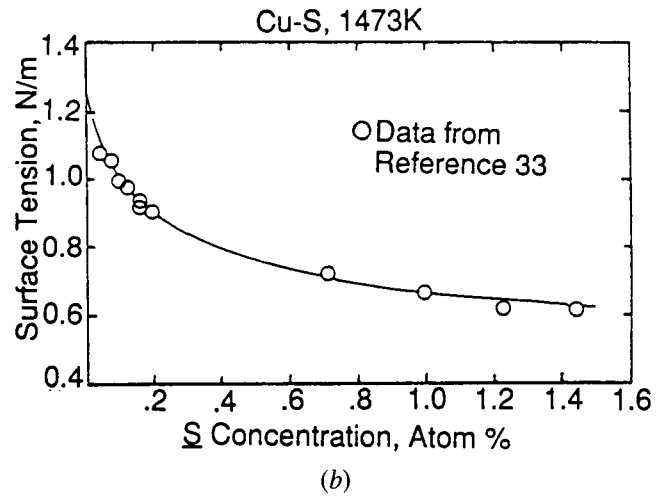
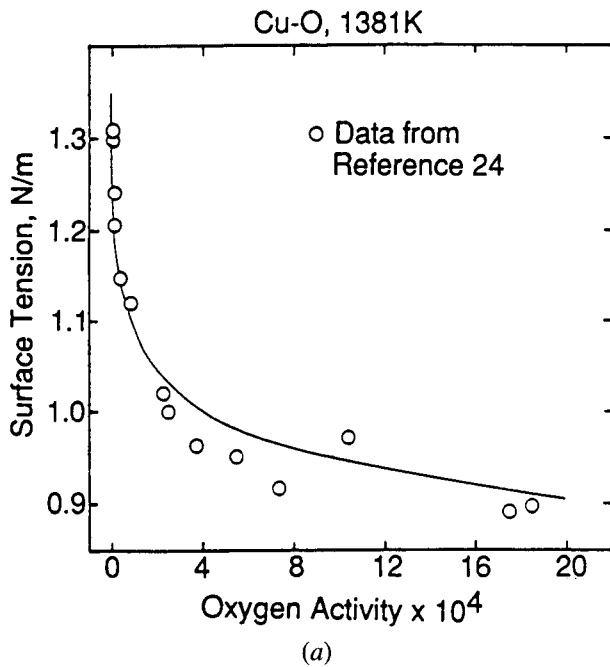


Fig. 3—Depression of surface tension of copper by (a) oxygen and (b) sulfur. The solid lines represent results calculated using Eq. [6]. The data points are taken from Refs. 24 and 33 for Cu-O and Cu-S systems, respectively.

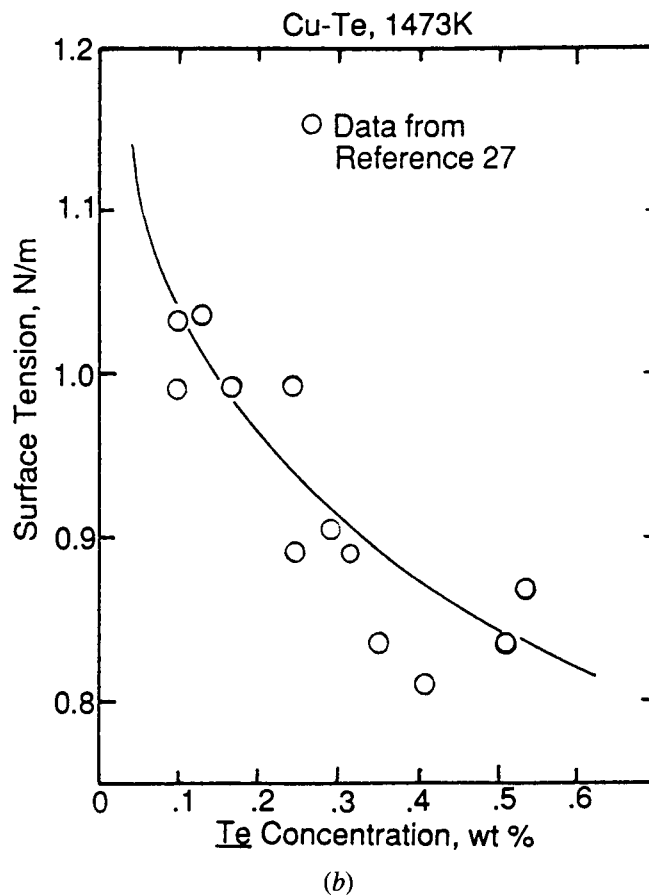
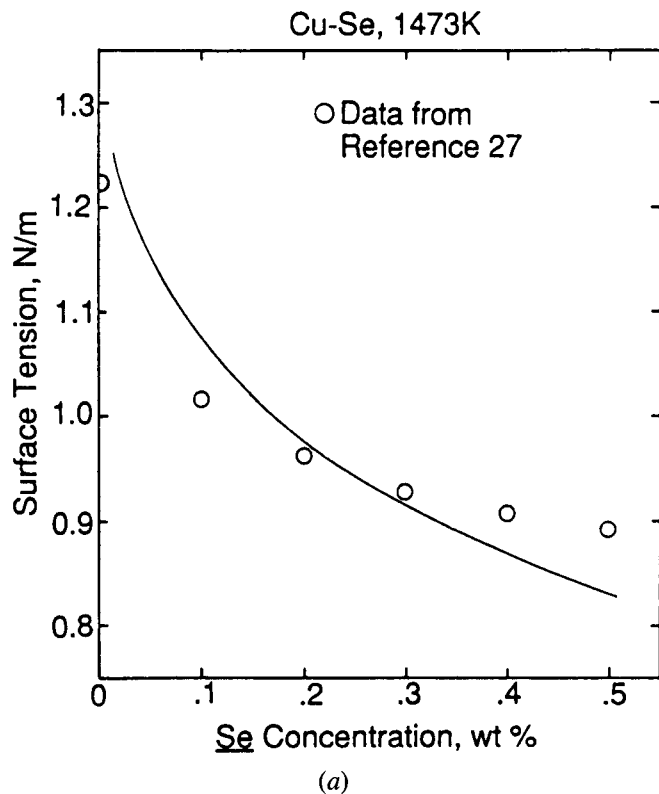


Fig. 4—Depression of surface tension of copper by (a) selenium and (b) tellurium. The solid lines represent results calculated using Eq. [6]. The data points are taken from Ref. 27.

Table III. Values Used in Calculating Surface Tension of Various Systems

System	$\gamma_m^\circ$ N/m	$A \times 10^4$ N/m K	$\Gamma_s \times 10^8$ Kg Mole/m <sup>2</sup>
Fe-O	1.943	4.3	2.03
Fe-S	1.943	4.3	1.30
Fe-Se	1.843	4.3	1.28
Cu-O	1.382	2.7	0.53
Cu-S	1.382	2.7	1.14
Cu-Se	1.382	2.7	1.4
Cu-Te	1.282	2.7	1.1
Ag-O	0.904	1.04	0.47

action between the solute and the solvent. Since the temperature dependence of interfacial tension is significantly influenced by  $\Delta H^\circ$ , we have tried to relate the values of  $\Delta H^\circ$  presented in Table II with various properties of the systems. It is difficult to draw truly general conclusions from this information, since all of the data available applies to transition metals and group VIB surface active solutes. However, these are the systems for which surface tension driven flow phenomena in welding would be of the greatest practical importance. In particular, we have attempted to seek correlations between the value of  $\Delta H^\circ$  and factors such as size difference, ion-ion attraction, and difference in electronegativity between the cation and the anion.

In plotting  $\Delta H^\circ$  as a function of the ionic size difference or as a function of the ion-ion attraction, no coherent trends

could be observed. This could possibly be due to the fact that such correlations do not take into account more complex interactions between the ions or the electronic distribution within the ions. However, by plotting  $-\Delta H^\circ$  as a function of the difference in electronegativity of the cation and the anion,<sup>[29]</sup> as shown in Figure 5, the results seem to indicate a small measure of correlation with significant scatter in the data.

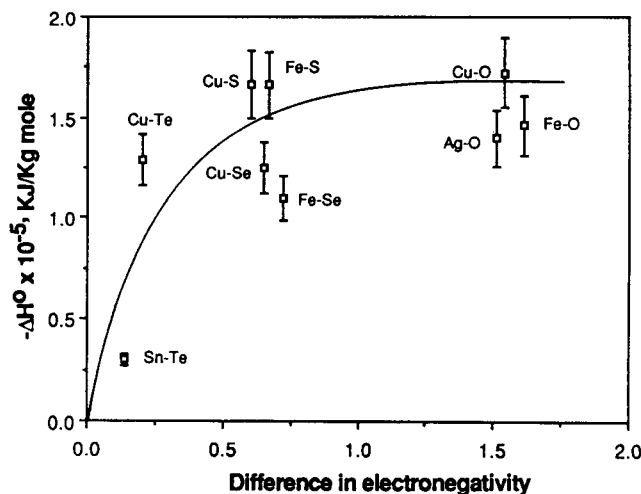


Fig. 5—Variation of the calculated heat of adsorption for various systems as a function of the difference in electronegativity of the solvent and solute ions.

It has been shown previously for silicate melts<sup>[13]</sup> that the heat of formation increases with the difference in electronegativity. From the works of Otsuka and Kozuka<sup>[14]</sup> it is observed that the heat of solution increases with the heat of formation. Since the heat of adsorption is the sum of the heat of solution and the heat of segregation, it is expected that the heat of adsorption should increase as the difference in electronegativity increases, as observed in Figure 5. The scatter in the plot indicates the complexity of the systems and emphasizes the fact that factors other than electronegativity are important in determining the heat of adsorption. However, when the difference in electronegativity is greater than about 0.5, the heat of adsorption lies between  $-1.21 \times 10^5$  and  $-1.72 \times 10^5$  KJ/Kg mole. These values are comparable with the heats of adsorption derived by Belton for the Fe-S, Cu-S, and Ag-O systems which are  $-1.47 \times 10^5$ ,  $-1.67 \times 10^5$ , and  $-2.0 \times 10^5$  KJ/Kg mole, respectively. This information is of particular interest for welding systems since the temperature coefficient of surface tension is significantly influenced by the heat of adsorption, and in most systems the difference in electronegativities is greater than 0.5 in Pauling's scale.

### B. Application to Other Systems

Surface tension was predicted for several systems in which very limited amount of experimental work has been done. In all the examples presented the values of  $k_1$  and  $\Delta H^\circ$  are not readily available. Because of this, the two parameters are estimated for each system based on certain simplifying assumptions and these are mentioned separately for each case.

#### 1. Cr-O

Nogi *et al.*<sup>[15]</sup> determined the surface tension of pure Cr as  $\gamma = 2.032 - 5.4 \times 10^{-4}(T - 2133)$  N/m and the surface excess at saturation,  $\Gamma_s$ , to be  $5.1 \times 10^{-9}$  Kg mole/m<sup>2</sup>. The heat of adsorption is taken equal to  $-1.67 \times 10^5$  KJ/Kg mole from the plot of Figure 5 with the difference in electronegativity taken as 1.78 in Pauling's scale. The value of  $k_1$  for the Cr-O system is taken to be the same as that for the Fe-O system since Fe and Cr are both transition metals. Based on these data, the interfacial tension of Cr-O system can be expressed as a function of temperature and composition as

$$\gamma = 2.032 - 5.4 \times 10^{-4}(T - 2133) - RT \times 5.1 \times 10^{-9} \ln[1 + 0.0138a_0e^{[(1.67 \times 10^8)/RT]}] \text{N/m} \quad [8]$$

Predictions of interfacial tension from the above equation were checked against the available experimental data of interfacial tension vs oxygen concentration at 1973 K.<sup>[15]</sup> It is observed from Figure 6(a) that good agreement is achieved between the experimental data and the predicted results.

#### 2. Co-S

Monma and Suto<sup>[16]</sup> have calculated  $\Gamma_s$  to be  $1.6 \times 10^{-8}$  Kg mole/m<sup>2</sup> and Nogi *et al.*<sup>[15]</sup> determined surface tension of pure cobalt as  $\gamma = 1.993 - 5.7 \times 10^{-4}(T - 1768)$  N/m. In the Co-S system the difference in electronegativity is equal to 0.62 and using this value, the heat of adsorption is interpolated from Figure 5 to be  $-1.55 \times 10^5$  KJ/Kg mole. The entropy factor  $k_1$  is assumed the same as for the

Fe-S system since both Co and Fe belong to the same group in the periodic table. Based on these simplifying factors, the surface tension relationship for the Co-S system was calculated as:

$$\gamma = 1.993 - 5.7 \times 10^{-4}(T - 1768) - RT \times 1.6 \times 10^{-8} \ln[1 + 0.00318a_0e^{[(1.55 \times 10^8)/RT]}] \text{N/m} \quad [9]$$

In Figure 6(b) the calculated values of surface tension are compared with the experimental data of Monma and Suto<sup>[16]</sup> at 1573 K as a function of sulfur concentration. It is observed that there is fair agreement between the predicted and experimental values.

#### 3. Ni-S

Surface tension of pure nickel has been calculated by Nogi *et al.*<sup>[15]</sup> as  $\gamma = 1.845 - 4.3 \times 10^{-4}(T - 1726)$  N/m and  $\Gamma_s$  has been calculated by Monma and Suto<sup>[16]</sup> to be  $1.6 \times 10^{-8}$  Kg mole/m<sup>2</sup>. From the difference in electronegativity values in this system (0.59) the heat of adsorption was interpolated from Figure 5 to be  $-1.47 \times 10^5$  KJ/Kg mole. The entropy factor was assumed the same as for the Fe-S system, since both nickel and iron interact in a similar way and belong to the same group in the periodic table. Based on these approximations, the surface tension of Ni-S system as a function of temperature and composition is given by

$$\gamma = 1.845 - 4.3 \times 10^{-4}(T - 1726) - RT \times 1.5 \times 10^{-8} \ln[1 + 0.00318a_0e^{[(1.47 \times 10^8)/RT]}] \text{N/m} \quad [10]$$

Figure 6(c) shows a plot of surface tension as a function of weight percent sulfur at 1573 K. Comparison of the predicted curve with the experimental values of Monma and Suto<sup>[16]</sup> show fair agreement.

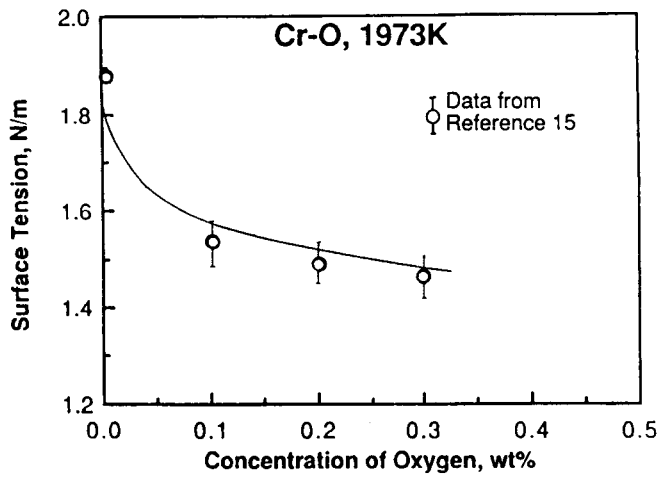
The study of the three systems mentioned above shows that in the absence of extensive experimental data in these systems it is possible to use Eq. [6] in combination with certain simplifying assumptions to predict the surface tension of these metal-solute systems.

### C. Temperature Coefficient of Surface Tension

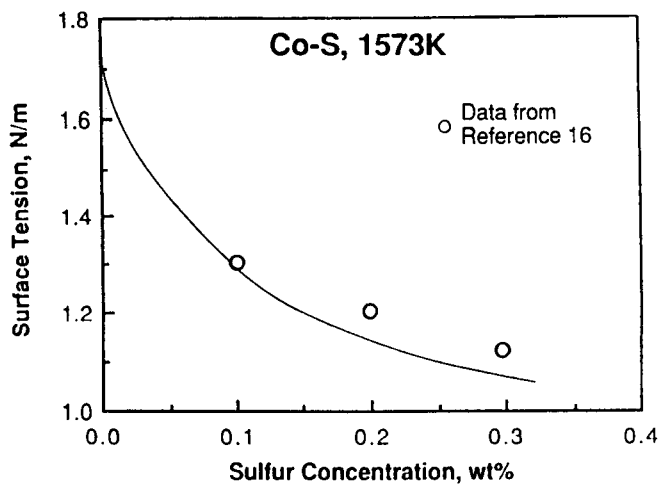
The value of  $d\gamma/dT$  can be obtained by differentiating Eq. [6] with respect to  $T$  as:

$$\frac{d\gamma}{dT} = -A - R\Gamma_s \ln(1 + Ka_i) - \frac{Ka_i}{(1 + Ka_i)} \frac{\Gamma_s(\Delta H^\circ - \Delta \bar{H}_i^M)}{T} \quad [11]$$

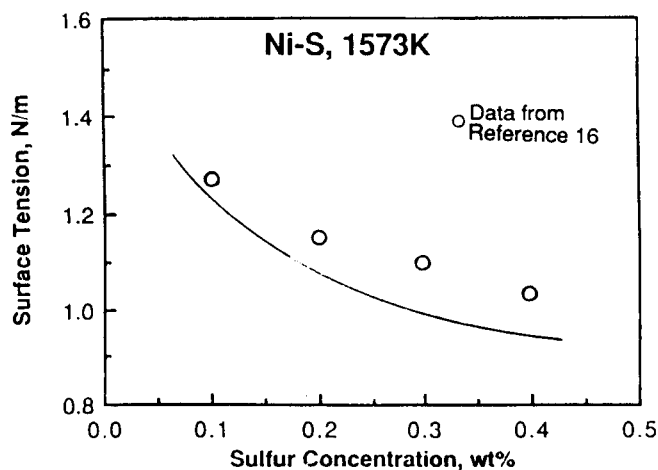
where  $\Delta \bar{H}_i^M$  is the partial molar enthalpy of mixing of species  $i$  in the solution. From Eq. [11] it is seen that  $d\gamma/dT$  is a function of both temperature and composition and is negative for pure metals. In alloys containing surface active solutes  $d\gamma/dT$  depends on temperature,  $T$ , the equilibrium constant for segregation,  $K$ , and the activity of the surface active species,  $a_i$ . For metals with a high surface coverage of the adsorbed species ( $Ka_i \gg 1$ ), Eq. [11] will reduce



(a)



(b)



(c)

Fig. 6—Calculated surface tension as a function of (a) oxygen concentration for Cr-O alloys, (b) sulfur concentration for Co-S alloys, and (c) sulfur concentration for Ni-S alloys. The solid lines represent predicted values using Eq. [6]. The data points are taken from Refs. 15, 16, and 16 for Cr-O, Co-S, and Ni-S systems, respectively.

to  $d\gamma/dT = -A - R\Gamma_s \ln(k_1 a_i) + \Gamma_s \Delta \bar{H}_s^M / T$ , and this value is usually negative. However, for metals with a low surface coverage of the surface active species ( $Ka_i \ll 1$ ), Eq. [11] will simplify to  $d\gamma/dT = -A - Ka_i \Gamma_s (\Delta H^\circ - \Delta \bar{H}_s^M) / T$ , and can be positive for a sufficiently large negative value of  $\Delta H^\circ$ . Under these conditions the Langmuir isotherm represents the effect of adsorbed atoms on the surface tension very well so that interactions between adsorbed atoms need not be considered. Increasing the temperature has the effect of causing adsorbed atoms to desorb from the surface, resulting in an increase in the surface tension. Therefore,  $\Delta H^\circ$ , the heat of adsorption of the surface active species at low surface coverages, is the most important parameter for determining the conditions under which the temperature coefficient of the surface tension can be positive.

The minimum activity of solute (O or S) required to obtain a positive value of  $d\gamma/dT$  at various temperatures can be calculated by equating  $d\gamma/dT$  to zero in Eq. [11]. For these calculations  $\Delta \bar{H}_s^M$  was taken as zero since the activity coefficients were taken to be unity. The calculated critical concentration values corresponding to these activities are presented in Figure 7 for Fe-O and Fe-S systems. It is observed that as the temperature increases, progressively larger amounts of the solute are required to produce a positive  $d\gamma/dT$ . In welding processes where the peak temperature is high, relatively high amounts of these surface active solutes will be required to ensure deep penetration of the weld.

Since a steep temperature gradient exists at the surface of a weld pool, calculations were carried out to examine how  $d\gamma/dT$  changes with temperature, given a particular amount of solute. Figures 8(a) and 8(b) show how  $d\gamma/dT$  varies with temperature at a given solute content for the Fe-O and Fe-S systems, respectively. In these figures the curves corresponding to higher concentrations of solute may intersect with each other; *i.e.*, a solution containing lower amounts of solute can have a higher  $d\gamma/dT$  than that for a solution having a higher concentration of the solute. Since the values of  $d\gamma/dT$  are contributed by the three terms in Eq. [11], the sign and magnitude of  $d\gamma/dT$  depend on the

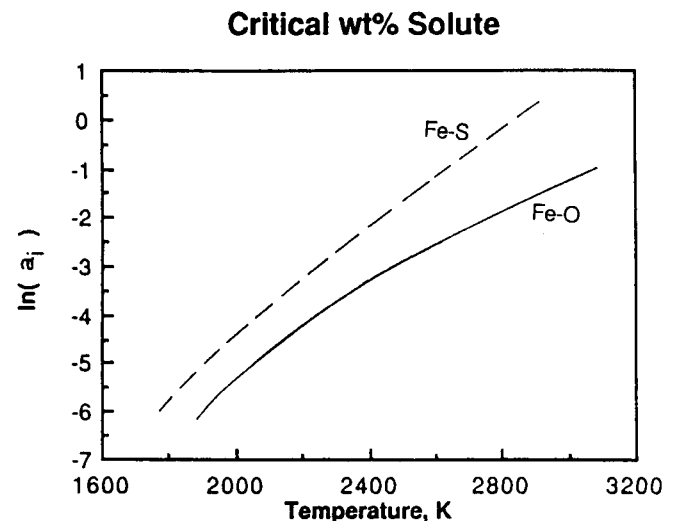
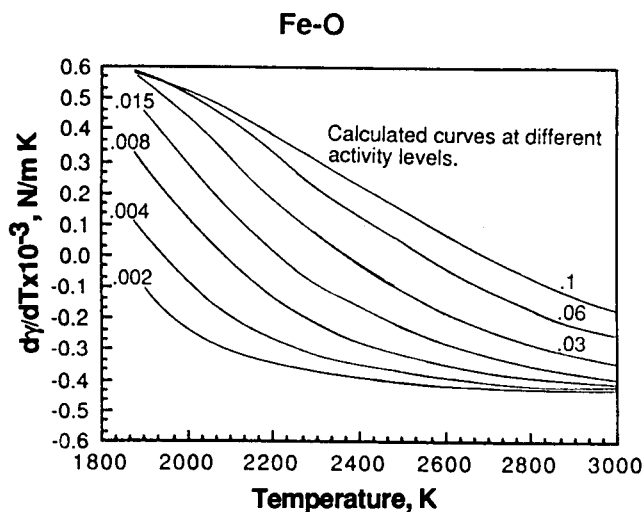
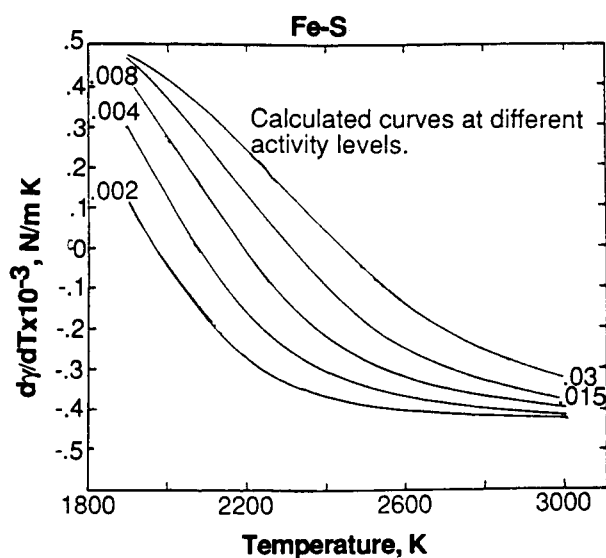


Fig. 7—The calculated critical solute content in Fe-solute systems as a function of temperature.



(a)



(b)

Fig. 8—Variation of temperature coefficient of surface tension of (a) Fe-O and (b) Fe-S systems as a function of composition and temperature.

relative values of these three terms. As the amount of solute in solution increases, the surface tension is lowered because more of the solute segregates to the surface. This means that the second term becomes larger in magnitude with increasing solute content. Also, this term is more important at lower temperatures, since at high temperatures the solute atoms tend to desorb. Thus, at relatively low temperatures, if the solute content is high, the large negative value of the second term dominates and  $dy/dT$  can be lower for a solution with high solute content as compared to one with a low solute content. However, with increase in temperature, the positive enthalpy term dominates and  $dy/dT$  will be higher for a solution with a higher solute content than for one with a lower solute content.

It is interesting to note that at very low oxygen contents (<0.002 wt pct),  $dy/dT$  will practically always be negative across the weld pool, whereas, at higher oxygen contents,  $dy/dT$  can change from a positive value at relatively low temperatures to a negative value at higher temperatures. A

similar trend is also observed for the Fe-S system. This implies that in a weld pool containing fairly high oxygen or sulfur contents,  $dy/dT$  may go through an inflection point somewhere on the surface of the pool. Under these conditions the fluid flow in weld pools is likely to be much more complicated than a simple recirculation.<sup>[20]</sup>

#### IV. CONCLUSIONS

From the analysis of the available interfacial tension data in Fe-O, Fe-S, Fe-Se, Cu-O, Cu-S, Cu-Se, Cu-Te, Ag-O, and Sn-Te systems, it is demonstrated that the interfacial tension in these systems could be satisfactorily described by a formalism based on the combination of Gibbs and Langmuir adsorption isotherms. Furthermore, interfacial tensions in Cr-O, Co-S, and Ni-S systems, predicted with some simplifying assumptions, agree fairly well with the limited amount of data reported in the literature. Calculations of temperature coefficients of interfacial tensions in Fe-O and Fe-S systems indicate that for these alloys,  $dy/dT$  can change from a positive value at relatively 'low' temperature to a negative value at 'high' temperatures when oxygen or sulfur is present at fairly high concentrations.

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