

# Communications

## Effect of Temperature and Composition on Surface Tension in Fe-Ni-Cr Alloys Containing Sulfur

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In many welding systems, the primary driving force for convection in the weld pool is the spatial gradient of interfacial tension that results from the temperature gradient at the weld pool surface. The intensity and the direction of the convection current and the accompanying heat transfer are influenced by the temperature coefficient of interfacial tension. The structure, properties, and chemical composition of the welds are strongly affected by heat transfer and metal flow in the weld pool and the alloying element loss from its surface. In many welding operations, the peak temperature in the weld pool can reach very close to the boiling point of the metal, and the weld metal is surrounded by plasma. Data on the temperature coefficient of surface tension for such high-temperature systems are scarce, if not unavailable.

Since the weld metals are exposed to a plasma environment during welding, the chemical natures of their surfaces are significantly different from that of most other metallic surfaces commonly encountered in extraction and refining processes. This difference can be observed from the lowering of both the interfacial tension<sup>[1]</sup> of metals and the vaporization rates of the metallic constituents in the alloys<sup>[2]</sup> in a plasma environment. Data on interfacial tension of important engineering alloys in the presence of plasma are not available in the literature. However, it has been recently demonstrated<sup>[1]</sup> that although the presence of plasma led to a lowering of interfacial tension of pure metals, the temperature coefficient of the interfacial tension was not affected.

When surface-active elements are present, the temperature coefficient of surface tension can become positive. In a previous article,<sup>[3]</sup> we have demonstrated that the surface tension of many binary metal-surface active solute systems can be adequately modeled on the basis of Gibbs and Langmuir adsorption isotherms and consideration of the surface segregation of the solutes. The dependence of the surface tension of a metal on both temperature and activity of a component is expressed by the equation

$$\sigma = \sigma^0 - A(T - T^0) - 8314T \Gamma_s \ln [1 + k a_s e^{-\Delta H^0/8.314T}] \quad [1]$$

where  $\sigma^0$  is the surface tension of the pure metal in N/m at a reference temperature  $T^0$ ,  $A$  is a constant which expresses the variation of surface tension of pure metal at

temperatures above the melting point in N/(m K),  $\Gamma_s$  is the surface excess in saturation in Kg mole/m<sup>2</sup>,  $k$  is the entropy factor,  $a_s$  is the activity of sulfur in the alloy, and  $\Delta H^0$  is the enthalpy of segregation in KJ/Kg mole. It was recently demonstrated<sup>[4,5]</sup> that a simple arbitrary assumption of a single valued positive  $d\sigma/dT$  leads to an unrealistic weld pool aspect ratio, whereas the use of Eq. [1] results in reliable predictions.

While mild steel can be adequately treated as a pure metal in which sulfur and oxygen are the only solute species which can influence the surface tension significantly, many important engineering alloys contain substantial quantities of alloying elements. The presence of these elements can also have a significant effect on the surface tension of the liquid metal and, as a consequence, on the welding behavior. An important group of such alloys is the austenitic stainless steels containing nickel, chromium, as well as smaller amounts of other elements. This article addresses the temperature and composition dependence of the surface tension of these alloys when sulfur is the primary surface-active impurity in the alloy.

Fundamentally, surface tension or surface energy results from the fact that atoms near a free surface have partially unfilled coordination shells which requires that they be at higher energy states than the atoms in the bulk of the solution. In a multicomponent alloy, atoms whose energy state is affected least by the surface are segregated to the surface region, and this reduces the magnitude of the surface energy. In metallic solutions, the group VI elements, oxygen, sulfur, selenium, and tellurium, are strongly surface active in spite of their low solubilities and therefore exert the strongest influence on the surface tension of the solution.<sup>[6]</sup> Metallic alloying elements can also be surface active, but because the magnitudes of the energy changes associated with the segregation of these elements are smaller, larger amounts of metallic species must be present to produce the same change in the surface tension of the solution.

A completely general formalism to determine surface tension of a multicomponent alloy containing a surface-active element would require a much more complex model than that represented by Eq. [1]. However, the behavior of some commercial alloys, such as stainless steel, may not require such a complex model, because in stainless steel, the principal metallic components of the alloy, nickel and chromium, are not strongly surface active. However, several issues must be examined for the application of an equation of a form similar to Eq. [1] to stainless steels, since they contain significant amounts of metallic alloying elements. The value of  $\sigma^0$ , the surface tension of the pure metal at a reference temperature in Eq. [1], must be replaced by a value for the pure metallic alloy. The value of  $A$ , the temperature coefficient of pure metal, must be determined for the alloy without the surface-active element. Finally, the effects of the metallic solutes on the segregation of the surface-active component must be addressed.

As a first step for the estimation of  $\sigma^0$  for Fe-Cr-Ni alloys, let us consider the behavior in the principal constituent binary systems, Fe-Cr and Fe-Ni. Yeum *et al.*<sup>[7]</sup> have developed a model to predict the surface tension of binary liquid metal alloys. The surface tension,  $\sigma_{AB}$ , and

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the surface composition of a pure metallic alloy,  $X'$ , without the surface-active elements can be calculated from the two simultaneous equations:

$$\sigma_{AB} = \sigma_A + \frac{RT}{S_A} \left[ \ln \frac{1 - X'_B}{1 - X_B} + \ln \frac{\gamma'_A}{\gamma_A} \right] \quad [2]$$

$$\sigma_{AB} = \sigma_B + \frac{RT}{S_B} \left[ \ln \frac{X'_B}{X_B} + \ln \frac{\gamma'_B}{\gamma_B} \right] \quad [3]$$

where  $\sigma_A$  and  $\sigma_B$  are the surface tensions of the pure elements,  $S_A$  and  $S_B$  are the surface areas of monolayers of the two elements in  $\text{m}^2/\text{gm atom}$ ,  $R$  is the gas constant,  $8.314 \text{ N m}/(\text{gm atom K})$ ,  $X_A$ ,  $X_B$ ,  $X'_A$ , and  $X'_B$  are the atom fractions of A and B in the bulk and the surface phases, respectively, and  $\gamma_A$ ,  $\gamma_B$ ,  $\gamma'_A$ , and  $\gamma'_B$  are the activity coefficients of the two components in the two phases. It should be noted that in the traditional treatment of interaction between gases and liquid alloys, no distinction is made between the surface and the bulk phases, and only one activity value is used for determining the equilibrium state of such systems. However, in Eqs. [2] and [3], the differences between the surface and the bulk compositions are recognized. If the pairwise interaction energies of atom pairs at the surface are assumed to be equal to that for the bulk phase, the sur-

face and the bulk values of the activity coefficients are related:<sup>[7]</sup>

$$\ln \gamma'_A = \frac{z'}{z} \ln \gamma_A \quad [4]$$

$$\ln \gamma'_B = \frac{z'}{z} \ln \gamma_B \quad [5]$$

for  $X'_B = X_B$ , where  $z$  and  $z'$  are the coordination numbers in the bulk and the surface, respectively. The activity coefficients,  $\gamma_A$  and  $\gamma_B$ , can be calculated from the excess partial molar free energy values,  $\bar{G}_A^{xs}$  and  $\bar{G}_B^{xs}$ , respectively. Thus, using Eqs. [2] through [5], the surface tension and the surface composition can be calculated as a function of the alloy composition.

Applying this approach to the Fe-Ni and Fe-Cr systems<sup>[8]</sup> leads to the results shown in Table I. Keene<sup>[9]</sup> has reviewed surface tension measurements for liquid binary iron alloys. The surface tensions of Fe-Ni and Fe-Cr systems show only a small dependence on composition. For Fe-Cr, Keene indicates that the surface tension decreases slightly with chromium content. For iron-nickel alloys, the behavior is similar, and recommended<sup>[9]</sup> surface tensions are given by  $\sigma_{\text{Fe-Ni}} = \sigma_{\text{Fe}} - 0.2X_{\text{Ni}}$ . This is in reasonable agreement with the values in Table I for Fe-Ni

Table I. Surface Properties of Binary Fe-Ni and Fe-Cr Alloys\*

Fe-Ni System							
$T = 1873 \text{ K}$							
$\sigma_A = 1.915 \text{ N/m}$							
$\sigma_B = 1.782 \text{ N/m}$							
$S_A = 3.68 \times 10^4 \text{ m}^2/\text{g} \cdot \text{atom}$							
$S_B = 3.54 \times 10^4 \text{ m}^2/\text{g} \cdot \text{atom}$							
$X_B$	$X'_B$	$\bar{G}_B^{xs} \text{ (J/mole)}$	$\bar{G}_A^{xs} \text{ (J/mole)}$	$\gamma_B$	$\gamma_A$	$\sigma_{\text{alloy}} \text{ (N/m)}$	
0.1	0.120	-6117	- 63	0.675	0.996	1.906	
0.2	0.236	-5745	- 121	0.691	0.992	1.896	
0.3	0.347	-5627	- 163	0.697	0.989	1.886	
0.4	0.455	-5288	- 351	0.712	0.978	1.876	
0.5	0.562	-4585	- 941	0.745	0.941	1.866	
0.6	0.667	-3439	- 2376	0.801	0.858	1.853	
0.7	0.769	-2041	- 4996	0.877	0.726	1.838	
0.8	0.860	- 887	- 8468	0.944	0.580	1.820	
0.9	0.937	- 209	-12,297	0.987	0.454	1.801	
Fe-Cr System							
$T = 1873 \text{ K}$							
$\sigma_A = 1.915 \text{ N/m}$							
$\sigma_B = 2.172 \text{ N/m}$							
$S_A = 3.68 \times 10^4 \text{ m}^2/\text{g} \cdot \text{atom}$							
$S_B = 3.44 \times 10^4 \text{ m}^2/\text{g} \cdot \text{atom}$							
$X_B$	$X'_B$	$\bar{G}_B^{xs} \text{ (J/mole)}$	$\bar{G}_A^{xs} \text{ (J/mole)}$	$\gamma_B$	$\gamma_A$	$\sigma_{\text{alloy}} \text{ (N/m)}$	
0.1	0.057	-2485	17	0.853	1.001	1.934	
0.2	0.119	-2590	33	0.846	1.002	1.956	
0.3	0.188	-2460	- 12	0.854	0.999	1.978	
0.4	0.265	-2159	- 180	0.871	0.989	2.002	
0.5	0.353	-1745	- 523	0.894	0.967	2.027	
0.6**	0.453	-1272	-1105	0.922	0.931	2.054	

\*All variables are explained in text.

\*\*Phase boundary

alloys. Because Fe, Ni, and Cr have very similar surface tensions and atomic dimensions and form nearly ideal solutions, the surface tension of a pure Fe-8 pct Ni-18 pct Cr alloy can be treated to be similar to that of pure Fe.

For a binary iron-chromium alloy, the temperature coefficient of surface tension,  $A$ , can be estimated from an expanded form of Eq. [2] in which  $\sigma_A$  is expressed as  $\sigma^0 + AT$ . We can rewrite Eq. [3] as

$$\sigma_{AB} = \sigma^0 + T \left[ A + \frac{R}{S_A} \left\{ \ln \frac{1 - X'_B}{1 - X_B} + \ln \frac{\gamma'_A}{\gamma_A} \right\} \right] \quad [6]$$

Therefore, the role of chromium in modifying the value of the temperature coefficient of surface tension, *i.e.*,  $A$  in Eq. [1], can be determined from the relative magnitudes of the two terms in the square bracket. Taking a value of  $S_A = 3.68 \times 10^4$  m<sup>2</sup>/gm mole and  $X_B = 0.2$ ,  $X'_B = 0.12$ , and  $\gamma'_A/\gamma_A = 1.0$  and  $A = 4.3 \times 10^{-4}$  N/m K, the value of the second term inside the square bracket is determined to be  $2.15 \times 10^{-5}$ . This value is only 5 pct of the value of  $A$ , the temperature coefficient for pure iron. Thus, the addition of chromium does not significantly affect the value of the temperature coefficient of surface tension. Similarly, it can be demonstrated that the addition of nickel to iron does not significantly affect the temperature coefficient of surface tension. The temperature coefficient of the Fe-Cr-Ni alloys can be taken to be equal to that for pure iron. This is consistent with the observation that the temperature coefficients of surface tension of Fe-Ni and Fe-Cr alloys are similar to that of pure iron.<sup>[9]</sup>

The next issue to be addressed is the influence of Cr and Ni on the segregation of sulfur to the surface. The segregation reaction may be written as



where  $\underline{S}$  represents the sulfur dissolved in liquid iron,  $V^s$  is an unoccupied surface site, and  $S^s$  is a surface site occupied by a sulfur atom. The standard Gibbs free energy change associated with Reaction [7] can be described by an enthalpy and an entropy term. The presence of Ni and Cr in the alloy can affect the segregation of sulfur by changing the entropy or the enthalpy of segregation of sulfur and/or changing the activity coefficient of sulfur in the bulk. The entropy decrease associated with the segregation of sulfur to the surface is unlikely to be significantly affected by the composition of the stainless steel surface to which it segregates. The enthalpy of segregation,  $\Delta H^0$ , is affected by the difference in electronegativity between the solvent and the surface-active solute. In binary systems, the heat of adsorption is approximately constant as long as the difference in electronegativity is greater than 0.5 volts, as is the case for sulfur<sup>[3]</sup> in Fe, Ni, and Cr. The heats of adsorption of sulfur in Ni and Cr are roughly equal, and the heat of adsorption of S in Fe is 10 pct higher than that in Ni and Cr. Therefore, the heat of adsorption of sulfur on pure iron can also be used for Fe-Ni-Cr alloys in the absence of more detailed data on the enthalpy of segregation of sulfur.

In dilute liquid iron-based alloys, the influence of Cr and Ni on the activity of S can be expressed through

their interaction parameters, which determine the activity coefficients of sulfur in liquid iron through Eq. [8].

$$\log f_s = e_s^{Cr} [\text{pct Cr}] + r_s^{Cr} [\text{pct Cr}]^2 + e_s^{Ni} [\text{pct Ni}] + r_s^{Ni} [\text{pct Ni}]^2 \quad [8]$$

The first- and second-order interaction coefficients in liquid iron are available in the literature.<sup>[10]</sup> The relevant data for the Fe-Cr-Ni-S system are summarized in Table II. Noting that the second-order interaction coefficient of Cr with S is zero and that there is no interaction between Ni and S, Eq. [8] reduces to

$$\log f_s = e_s^{Cr} [\text{pct Cr}] \quad [9]$$

and the activity of sulfur in Eq. [1] is given by

$$a_s = [\text{pct S}] 10^{[e_s^{Cr} [\text{pct Cr}]]} \quad [10]$$

Since nickel does not interact with sulfur in iron, the surface tension of an Fe-Ni alloy containing sulfur would be expected to be the same as that of iron with the same sulfur content. The surface tension of molten stainless steel containing sulfur would be expected to differ from that of pure iron containing the same concentration of sulfur, because chromium modifies the activity coefficient of sulfur. Figure 1 shows the calculated surface tension of stainless steel containing 18 pct Cr as a function of temperature and [pct S] along with the calculated surface tension of a binary Fe-S alloy for comparison. Until up to about 2400 K, the surface tension of the chromium-containing alloy will be somewhat higher than that for the binary Fe-S alloy. At higher temperatures, the activity coefficient of sulfur becomes positive, and as a result, the calculated values of surface tension of Fe-Cr-Ni-S alloys are slightly lower than for the binary Fe-S alloys.

The most important parameter in welding applications is the temperature coefficient of surface tension of the alloy. This can be obtained by differentiating Eq. [1] while taking into account the temperature variation of the activity coefficient of sulfur defined by Eq. [10].

$$\frac{d\sigma}{dT} = -A - 8314T\Gamma_s \ln(1 + k a_s) - \frac{k a_s \Delta H^0 \Gamma_s}{T(1 + k a_s)} \quad [11]$$

Figure 2 shows the calculated temperature coefficient as a function of temperature for several sulfur concentrations. Near the melting point, the values for the Fe-Cr-Ni-S alloys are slightly smaller than that for the binary Fe-S alloys. However, at higher temperatures, the difference is insignificant. The surface tension data

**Table II. Thermodynamic Data for Dilute Fe-Cr-Ni-S Alloys**

1. Solution of S in iron: $1/2S_2(g) = \underline{S} \quad \Delta G^0 = -32,280 + 5.6T(\text{cal/mole})$
2. Interaction of Cr with S in iron: $e_s^{CrS} = -94.2/T + 0.0396$ (first order) $r_s^{CrS} = 0$ (second order)
3. Interaction of Ni with S in iron: $e_s^{NiS} = 0$

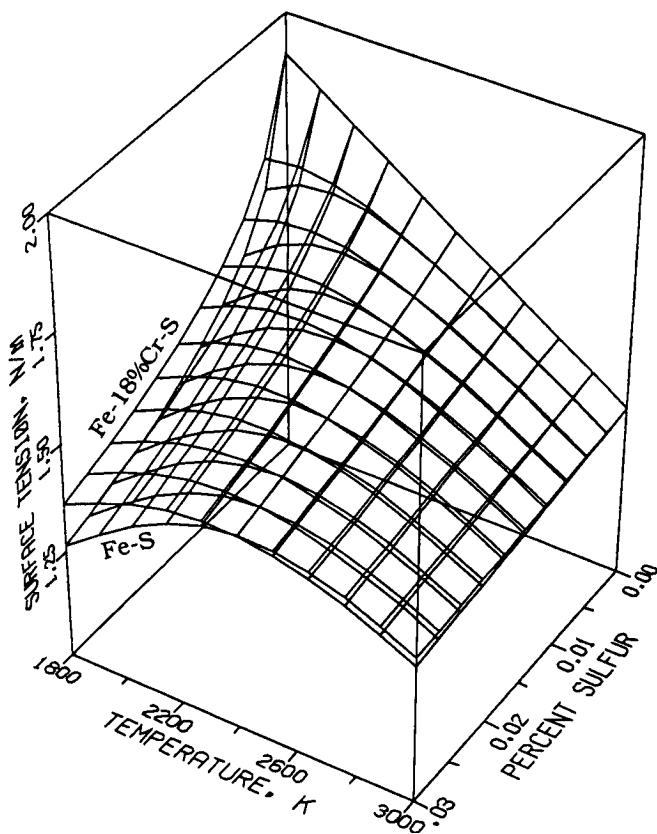


Fig. 1—Surface tension of Fe-S and Fe-8 pct Ni-18 pct Cr-S alloys as a function of temperature and sulfur concentration.

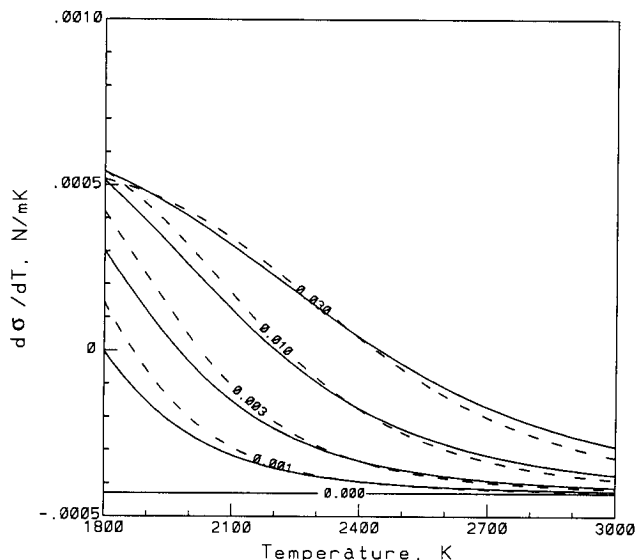


Fig. 2—Variation of the temperature coefficient of surface tension,  $d\sigma/dT$ , as a function of temperature and sulfur concentration. The solid lines represent the Fe-8 pct Ni-18 pct Cr-S alloy, and the dashed lines represent the binary Fe-S alloys. The numerical values on the curves are the weight percent sulfur values.

for the Fe-Ni-Cr-S system in the temperature range of interest in welding are not available. In view of the lack of data and the calculations presented in this communication, theoretical investigations of heat transfer and fluid flow in a stainless steel weld pool can be under-

taken using the temperature coefficient of surface tension values for the Fe-S system.

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## Chemical Vapor Deposition Kinetics of Tungsten from $WCl_6$ onto Nickel Plate at Elevated Temperatures

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Chemical vapor deposition (CVD) is used to place a protective surface coating on materials in order to improve their physical, chemical, and/or mechanical properties.<sup>[1]</sup> Tungsten is used widely for coating semiconductors and heat- and wear-resistant materials. Much work has been done on the thermodynamics and phenomenology of tungsten CVD, but the rate processes involved have not been studied extensively. This work was concerned with measuring the kinetics and determining the rate-controlling steps for W deposition on nickel substrate by the vapor-phase reduction of  $WCl_6$  by  $H_2$ .

The impurity contents in the nickel used in this work are given in Table I. The substrate surface was

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