STICT Model for Surface Thermodynamics of Liquid Metal Solutions

A new model, called STICT for surface thermodynamics using ideal chemical theory, is developed for the surface tension of liquid metal alloys. It uses the Guggenheim approach to relate surface phase properties to those in the bulk. For strongly solvated metal mixtures, ideal chemical theory is used to characterize bulk properties. The STICT model fits experimental data well for the seven systems for which sufficient data exist. Moreover, calculations of bulk and surface true compositions give some guidance to the tailoring of the surface properties of alloys for various applications.

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Introduction

Knowledge of the surface thermodynamics of liquid metal solutions is important in a number of advancing technologies. Important applications include the use of liquid metal solvents for the carbothermic reduction of metal oxide ores (Anderson, 1970; Anderson and Parlee, 1974, 1976; Bakshani, 1977; Graves, 1978; Krikorian, 1979; Lira, 1984), the production of fiber-reinforced metals (Kingery, 1953; Humenik and Kingery, 1954; Humenik and Parikh, 1956; Thomas et al., 1963; Kelly, 1964; Kelly and Davies, 1965a,b; Manning and Stoops, 1968; Humenik, 1973), and the fabrication of equipment requiring ceramic-to-metal bonding (Williams and Nielsen, 1959; MacKenzie, 1984; Morgan et al., 1982). Because of their high interfacial energies, most liquid metals do not significantly wet many solid surfaces. This leads to unacceptably slow kinetics for some carbothermic reductions and poor bonding of the fiber and metal constituents in composite materials and ceramic-to-metal bonds. The development of these technologies requires enhanced wetting of the solid by the liquid metal.

Enhanced wetting can be achieved by modifying the solid or liquid surfaces or a combination of both. Since the surface properties of liquids can be influenced easily by the addition of small amounts of surface-active components, it is this method that shows the greatest promise in furthering the development of the aforementioned technologies. Many liquid metal solutions exhibit evidence of intermetallic compound formation. Compound formation many times leads to a lowering of the surface tension and lower surface tension usually results in enhanced wetting. Therefore, it is postulated that enhanced wetting by liquid metals can be achieved by the addition of small amounts of second components that form intermetallic compounds with the primary component.

There is extensive evidence of intermetallic compound formation in liquid metal solutions (Wilson, 1965; Steeb and Entress, 1966; Steeb and Hezel, 1966; Bhatia and Thornton, 1970; Bhatia et al., 1974a,b; Shimoji, 1978; Jordan, 1979; Predel, 1979; Chieux and Ruppersberg, 1980; Stoicos, 1980; Sommer, 1982b), and "chemical" solution theories acknowledging such behavior have been quite successful in modeling liquid alloy properties (Hildebrand and Eastman, 1915; Jordan, 1970, 1976; Bhatia et al., 1974a,b; Bhatia and Ratti, 1977; Predel and Oehme, 1976; Eckert et al., 1982; Sommer, 1982a,b; Alger and Eckert, 1983). We postulate that similar compound formation occurs in the surface phase, and an example substantiating such a phenomenon is shown in Figure 1, where a minimum in surface tension occurs at the same composition as the very strong intermetallic compound Zn_2Mg. In this paper we apply the ideal chemical theory (ICT) model as developed by Alger and Eckert (1983) to the surface phase thermodynamics of liquid alloys. The model is capable of accurately representing the surface tension isotherm of compound-forming solutions with a minimum number of parameters. The model parameters are based on well-defined, physically meaningful thermodynamic properties. In addition, the model is capable of qualitatively predicting the general shape of the isotherm knowing only bulk phase and pure-component surface properties. This is the first application of chemical theory to modeling the surface thermodynamics of solutions known to the authors.

Surface Phase Thermodynamics

A number of investigators have directed their efforts at modeling the surface thermodynamics of liquid metal solutions, for example, the work of Taylor (1956), Hoar and Melford (1957), Kaufman (1967), Laty et al. (1976), Bhatia and March (1978),

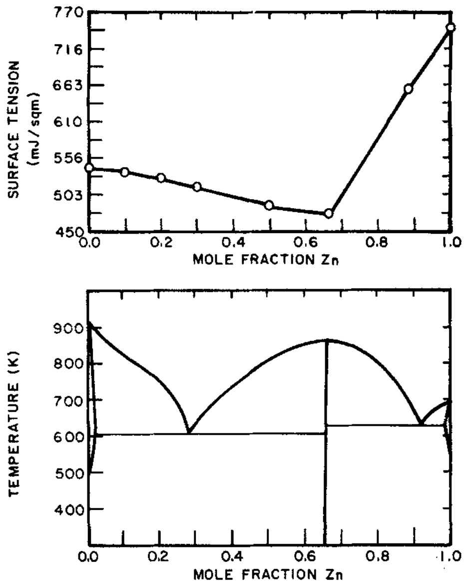

**Figure 1. Top: Surface tension isotherm at 973 K for Zn-Mg system.
Bottom: Simplified equilibrium phase diagram for Zn-Mg system.**

Okajima and Sakao (1982), and Angal and Roy (1982). These investigations are reviewed in detail elsewhere (Howell, 1986), but two points are important:

1. Modeling chemical interactions is important for systems that show evidence of compound formation.
2. Quantitative agreement between predicted and experimental surface tension isotherms is possible only when adjustable parameters are introduced to account for important interactions that are not included explicitly in the simple model. These parameters should represent physically realistic quantities; quantities that are not measured directly, but have physical meaning.

We propose the STICT (surface thermodynamics using ideal chemical theory) model, developed as follows: consider a closed system in equilibrium containing two homogeneous bulk phases separated by a common planar surface phase. Neglecting magnetic and gravitational energies, the energy content of the system can be increased in only three ways, namely the supply of heat, PV work, and surface work. The surface work is the work necessary to increase the surface area through the transport of species from a bulk phase to the surface phase. Eriksson (1964) has shown that the relationship between the chemical potential of a component in the surface phase to its chemical potential in a bulk phase is represented by the following equation

$$\mu_i^s = \mu_i^b + A_i \sigma \tag{1}$$

This relationship assumes that the surface phase is characterized by a monolayer and that the partial molar area of a component in the solution is equal to its molar area.

In modeling the surface thermodynamic properties of liquid metal solutions, the description of the surface phase as a single monolayer is not considered to be severe. Rice and coworkers (D'Evelyn and Rice, 1983a,b; Sluis et al., 1983; Sluis and Rice, 1983; Gryko and Rice, 1984) have shown recently that simple liquid metal surfaces, unlike those of dielectric liquids, exhibit atomic-scale layering. In addition, Prigogine and Defay (1954) showed that the surface tension calculated from a two-layer model differed little from the monolayer model surface tension.

In order to make Eq. 1 useful for dealing with experimental data it is necessary to relate the chemical potential to activities. The activity of a component in a uniform bulk phase is introduced by

$$\mu_i^b = \mu_i^{0b} + RT \ln a_i^b \tag{2}$$

Assuming that an analogous relation exists for the surface phase, the activity of a component in the surface phase is introduced by

$$\mu_i^s = \mu_i^{0s} + RT \ln a_i^s \tag{3}$$

The bulk phase activity can be expressed as the product of the true mole fraction, z_i, and the true activity coefficient, α_i. Assuming that an analogous expression is applicable for the surface phase activity, Eqs. 1, 2, and 3 can be combined to give

$$\sigma = \sigma_i^0 + \frac{RT}{A_i} \ln \frac{z_i^s \alpha_i^s}{z_i \alpha_i} \tag{4}$$

where use has been made of the fact that the pure substance is the standard state, i.e.,

$$\mu_i^{0s} - \mu_i^{0b} = A_i \sigma_i^0 \tag{5}$$

Rearrangement of Eq. 4 results in the following

$$z_i^s = z_i \frac{\alpha_i}{\alpha_i^s} \exp\left[\frac{(\sigma - \sigma_i^0) A_i}{RT}\right] \tag{6}$$

This equation relates the surface true mole fraction to the bulk true mole fraction of component i. The general form of Eq. 4 is obtained by multiplying the expression for each component by its surface true mole fraction and adding the results

$$\sigma = \sum_{i=1}^{N} \sigma_i^0 z_i^s + RT \sum_{i=1}^{N} \frac{z_i^s}{A_i} \ln \frac{z_i^s \alpha_i^s}{z_i \alpha_i} \tag{7}$$

where N is the total number of components.

Equations 6 and 7 are the fundamental equations describing the surface thermodynamics based on chemical theory.

Many liquid metal solutions exhibit large negative deviations from ideal behavior and show evidence of very strong compound formation. Thus the chemical interactions are dominant and the physical interactions may be neglected in the ICT bulk solution model. In comparison, organic solutions do not usually exhibit such extreme behavior and probably need to be modeled using either physical models or chemical-physical models. Moreover, in liquid metals, assumptions of spherically symmetric forces are generally valid, whereas in complex organic systems, especially at an interface, both asymmetry and orientation are certainly factors. Due to the two-dimensional nature of the surface region, physical interactions may be less important at the surface than in the bulk phase (Taylor, 1956). Therefore, if physical interactions are neglected in modeling the bulk phase thermodynamics of certain liquid metal solutions, the assumption of an ideal surface phase is valid. When the bulk and surface phases are ideal the true activity coefficients of each of the components equal one. Equations 6 and 7 can then be simplified

$$z_i^s = z_i \exp\left[\frac{(\sigma - \sigma_i^0)A_i}{RT}\right] \tag{8}$$

$$\sigma = \sum_{i=1}^{N} \sigma_i^0 z_i^s + RT \sum_{i=1}^{N} \frac{z_i^s}{A_i} \ln \frac{z_i^s}{z_i} \tag{9}$$

These equations constitute the STICT model. We assume that the bulk solution thermodynamics are known and may be analyzed for the equilibrium constants for compound formation and thus the composition variation of the bulk true solution. We assume also that the pure-component surface tensions for the monomers are available, so that the only unknowns in the above equations are the surface tensions of the intermetallic compounds and the molar areas of the components in the solution. The surface tensions of the compounds are the adjustable parameters and the molar areas are determined from the pure-component volumes and experimental excess volume data.

For a given set of σ_i^0 for the compounds, Eq. 9 can be solved uniquely for σ. Therefore, the best fit of experimental surface tension data can be obtained by minimizing the objective function θ

$$\theta = \sum_{\text{all data}} \left[\frac{\sigma^{\text{exp}} - \sigma(\sigma_i^0)^{\text{calc}}}{\sigma^{\text{exp}}}\right]^2 \tag{10}$$

The fitting of the STICT model is an optimization in N-2 dimensions, equal to the number of compounds.

Determination of the Molar Areas

The molar areas of the components in the liquid metal true solution are determined from the molar volumes of the monomers and the excess volume isotherm. Since this model is based on a monolayer surface phase the appropriate area to use is the projected area. For models not based on a monolayer surface phase the choice of which area to use in calculating the molar areas is not straightforward (Hoar and Melford, 1957; Eriksson, 1964). Assuming that both the monomers and the compounds are approximately spherical, the projected molar area is calculated by

$$A_i = (N_{AV}\pi)^{1/3} (3/4)^{2/3} (v_i)^{2/3} \tag{11}$$

where N_{AV} is Avogadro's number and v_i is the molar volume of component i. The molar volumes of the monomers are determined experimentally; molar volumes for the compounds are found from excess volume data, if available, by the method of Lira (1986), or if unavailable, a zero excess volume is assumed. Results are quite insensitive to small variations in the volumes, or projected areas.

Application of STICT Model

The STICT model was used to fit the experimental surface tension isotherms of seven liquid metal systems. These are the only systems for which the necessary experimental data are available and the assumptions of ICT may be valid. Using ICT and the method developed by Alger and Eckert (1983), the bulk activity coefficient data are used to determine the number and stoichiometry of the compounds existing in solution and the composition variation of the bulk true solution. The excess volume data are used when available to determine the molar areas of the compounds. The STICT model relates the surface true solution thermodynamic properties to the bulk true solution thermodynamic properties. The sources of the data for the systems investigated are shown in Table 1.

The STICT model uses the surface tensions of the compounds that are assumed to exist in the bulk solution as parameters in fitting the experimental surface tension isotherm. The equilibrium constants are not adjustable parameters in the STICT model; they result from a fit of bulk phase data. Only the components present in the bulk phase are assumed to exist in the surface phase. Therefore, the number and type of parameters used in the STICT model are fixed by the bulk phase ICT model.

Table 2 shows the input data for the compounds used in the STICT model for the seven systems. In general, the greater the equilibrium constant the stronger the compound and the greater its effect on the solution properties. Therefore, the Cd-Sb, Mg-Sn, and Cu-Al systems exhibit the strongest effects of compound formation.

Table 3 lists the surface tensions of the pure components at the isotherm temperature, the value of the model parameters, i.e., the surface tensions of the compounds, and the mean errors of fit for the calculated isotherms. Based on the pure-component surface tensions, the mean errors of fit are all less than 1.5%. This is much better than the fit obtained by previous models for compound-forming systems.

The excess surface tension provides a more stringent test of both the fit of the calculated isotherm and the precision of the experimental data. The excess surface tension, as defined by Eckert and Prausnitz (1964), is given by

$$\sigma^E = \sigma - x_1\sigma_1^0 - x_2\sigma_2^0 \tag{12}$$

Scatter in the experimental data is amplified when plotted as the excess surface tension, and the isotherm shows more clearly the effects of compound formation. However, any errors in either the calculated or experimental data appear much greater for systems with approximately linear surface tension isotherms when compared to systems with highly nonlinear isotherms. The

Table 1. Experimental Data Sources

System	Activity Coeff.	Excess Volume	Surface Tension Isotherm
Pb-Bi	Alger (1982)	Kazakova et al. (1984)	Kazakova et al. (1984)
Pb-Sb	Hultgren et al. (1973)	Greenaway (1948)	Matuyama (1927)
Cd-Sb	Hultgren et al. (1973)	No data available	Greenaway (1948)
In-Sb	Hultgren et al. (1973)	No data available	Lazarev (1964)
Mg-Sn	Irwin (1978)	Faxon (1966)	Eremenko et al. (1977)
Zn-Mg	Hultgren et al. (1973)	Pelzel & Sauerwald (1941)	Pelzel & Sauerwald (1941)
Cu-Al	Perakis et al. (1973)	Bornemann & Sauerwald (1922)	Eremenko et al. (1961)

Table 2. Input Data for Compounds Used in STICT Model

System	Compounds	Equilib. Constant	Molar Area $10^5 \times m^2/mol$	Temp. K
Pb-Bi	PbBi	1.69*	1.192	673
Pb-Sb	PbSb	0.27**	1.173	908
Cd-Sb	CdSb	2.34**	1.021	773
	Cd_3Sb_2	39.46**	1.846	
In-Sb	InSb	3.72*	1.096	973
	In_3Sb	4.94*	1.715	
Mg-Sn	MgSn	65.44*	1.019	1,073
	Mg_2Sn	271.7*	1.327	
Zn-Mg	ZnMg	3.43**	0.817	973
	Zn_2Mg	2.23**	1.079	
	Zn_5Mg	7.11**	1.583	
Cu-Al	CuAl	24.01†	0.708	1,373
	Cu_3Al	241.8†	1.003	
	Cu_3Al_2	683.1†	1.031	

*Fit by Alger (1982)
**Fit by authors, using activity coefficient data of Hultgren et al. (1973)
†Fit by Lira (1982)

precision of most experimental liquid metal surface tension data is only 1 to 2%, or approximately 10 mJ/m^2 for many liquid metals. This should be kept in mind when comparing excess surface tension isotherms for different systems.

Figures 2 to 5 are plots of the excess surface tension and surface tension isotherms for four of the systems investigated. The circles are the experimental data points and the solid curves are the isotherms calculated from the STICT model. The bars on the first excess surface tension data points represent the approximate experimental error discussed above. The error bars are provided to help compare the four systems. In all four cases shown, as well as for the other systems investigated, the STICT model fits the data within experimental uncertainty.

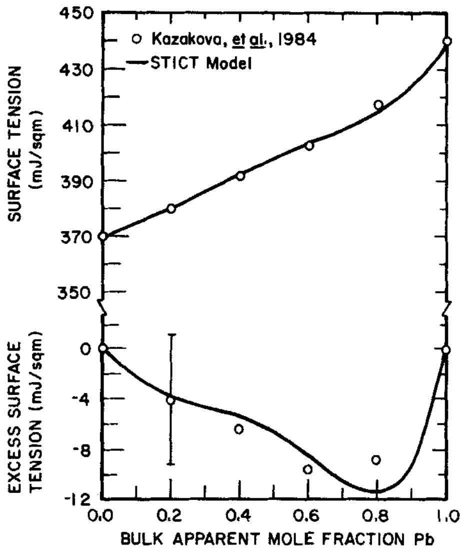

Figure 2. STICT model fit for Pb-Bi system at 673 K.
Surface tension and excess surface tension isotherms

Figure 2 shows the Pb-Bi system at 673 K. One compound, PbBi, is assumed to exist in the solution with an equilibrium constant of 1.69, and the surface tension of the compound fit is 403 mJ/m^2. Because the equilibrium constant is small the effect of compound formation on the isotherm is weak.

Table 3. STICT Model Parameters and Mean Error of Fit

System A-B	Pure-Component Surface Tension mJ/m^2 A	B	Compounds	Compound Surface Tension (mJ/m^2)	Mean Error of Fit (mJ/m^2)
Pb-Bi	441	370	PbBi	403	1.2
Pb-Sb	461	367	PbSb	379	2.6
Cd-Sb	607	380	CdSb	568	2.4
			Cd_3Sb_2	492	
In-Sb	513	350	InSb	434	5.1
			In_3Sb	467	
Mg-Sn	550	501	MgSn	530	4.1
			Mg_2Sn	527	
Zn-Mg	750	542	ZnMg	752	2.8
			Zn_2Mg	895	
			Zn_5Mg	653	
Cu-Al	1,343	810	CuAl	1,113	12.1
			Cu_3Al	1,106	
			Cu_3Al_2	916	

A more interesting system from the standpoint of the effect of compound formation is the Cd-Sb system. The STICT model fit at 773 K is shown in Figure 3. This is a two-compound system, with the compounds having stoichiometries of CdSb and Cd_3Sb_2. The equilibrium constants are 2.34 and 39.46, and the surface tensions are 568 and 492 mJ/m^2, respectively. The second, stronger compound causes a change in the curvature of the calculated surface tension isotherm, i.e., a perturbation, near the stoichiometric composition of the compound. This effect is also shown clearly in the excess surface tension isotherm where a perturbation exists in the composition range of $x_{Cd} = 0.5$ to 0.8. The perturbation in either isotherm is not centered on the stoichiometric composition of the compound, but rather shifted toward the pure component with the greater surface tension. The reason for this will be discussed below.

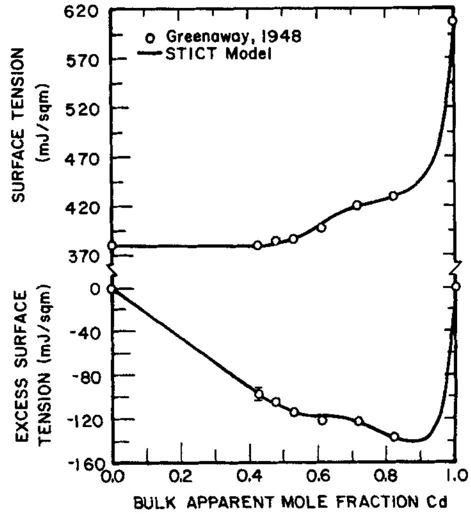

Figure 3. STICT model fit for Cd-Sb system at 773 K.
Surface tension and excess surface tension isotherms

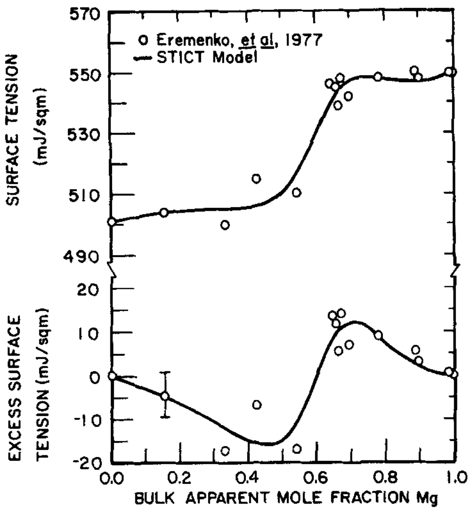

Figure 4. STICT model fit for Mg-Sn system at 1,073 K.
Surface tension and excess surface tension isotherms

The Mg-Sn system, Figure 4, is modeled assuming two compounds, MgSn and Mg_2Sn. The equilibrium constants at 1,073 K are $K_{MgSn} = 65.44$ and $K_{Mg_2Sn} = 271.7$. The surface tension of the MgSn compound is 530 mJ/m^2 and the Mg_2Sn compound is 527 mJ/m^2. Because both compounds have large equilibrium constants the surface tension isotherm is affected dramatically. The curvature of the isotherm changes sign twice within the region $x_{Mg} = 0.4$ to 0.8. The excess surface tension isotherm exhibits extrema at approximately the stoichiometric compositions of the two compounds. The two extrema are not shifted markedly because the two pure-component surface tensions are not significantly different.

Figure 5 shows the excess surface tension and surface tension isotherms for the Cu-Al system at 1,373 K. Three compounds are required to model accurately the bulk solution thermodynamics, CuAl, Cu_3Al, and Cu_3Al_2. The equilibrium constants are $K_{CuAl} = 24.01$, $K_{Cu_3Al} = 241.8$, and $K_{Cu_3Al_2} = 683.1$. The surface tensions of the compounds fit are $\sigma_{CuAl} = 1{,}113$ mJ/m^2, $\sigma_{Cu_3Al} = 1{,}106$ mJ/m^2, and $\sigma_{Cu_3Al_2} = 916$ mJ/m^2. The effect of compound formation on the surface tension isotherm is apparent in the composition range $x_{Cu} = 0.6$ to 0.9. A large perturbation in the isotherm is exhibited. The excess surface tension shows a maximum in this range. As with the Cd-Sb system, the perturbation is shifted toward the pure component having the greater surface tension.

Bulk and Surface Composition Variations

The STICT model also shows how the bulk true solution composition influences the surface tension isotherm. An ICT fit of the bulk apparent activity coefficients provides a relationship between the bulk true mole fractions and the bulk apparent mole fractions. From a knowledge of the bulk true solution composition and the surface tensions of the monomers and intermetallic compounds, the surface true solution composition can be determined using Eq. 8, and the surface tension isotherm using Eq. 9. Therefore, within the framework of chemical theory, variations in the surface tension isotherm can be viewed as a result of composition variations in the bulk true solution. This is supported by the relationship between the presence of perturbations in the isotherm and the number and strength of the compounds as presented in the previous section. The relationship between the bulk true solution and the surface true solution will be illustrated for two liquid metal systems, Mg-Sn (two compounds), and Cu-Al (three compounds).

Figure 6 shows the plots of the bulk and surface true solution composition variations for the Mg-Sn system at 1,073 K. The bulk compound true mole fraction reaches a maximum at the composition equal to its atomic constitution. The large equilibrium constants for this system ($K_{MgSn} = 65.44$ and $K_{Mg_2Sn} = 271.7$) indicate that the extent of compound formation is significant. In the bulk apparent composition range of $x_{Mg} = 0.4$ to 0.8 both the bulk and surface phases are composed largely of the compounds. This leads to the existence of a perturbation in the surface tension isotherm in this composition range. The surface phase composition variation is not greatly different from the variation in the bulk phase. The surface phase shows only a slight enrichment in the apparent component with the lower surface tension, i.e., tin. This is because the surface tension of mag-

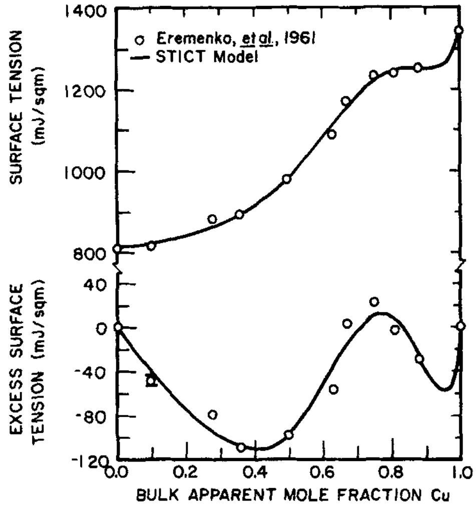

Figure 5. STICT model fit for Cu-Al system at 1,373 K.
Surface tension and excess surface tension isotherms

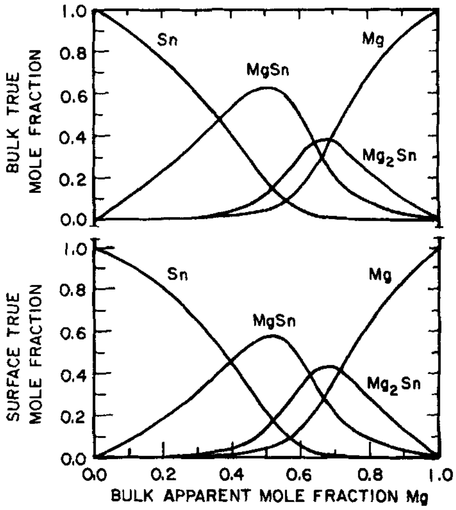

Figure 6. Bulk and surface true composition variation for Mg-Sn system at 1,073 K.

nesium, 550 mJ/m^2, is not significantly different from the surface tension of tin, 501 mJ/m^2. The surface true composition variation for a system where the surface tensions of the pure components are quite different will be shifted greatly away from the pure component with the lowest surface tension. This type of behavior is exhibited by the Cu-Al system.

Figure 7 shows the bulk and surface phase true composition variations for the Cu-Al system at 1,373 K. The surface tension of pure copper is 1,343 mJ/m^2 and that of pure aluminum is 810 mJ/m^2. The difference between the two surface tensions is 533 mJ/m^2. As shown in the bottom plot of Figure 7, this large difference causes the surface to be enriched in the element with the lower surface tension: aluminum. The bulk true solution exhibits strong compound formation in the approximate range $x_{Cu} = 0.35$ to 0.65, while the composition range for strong compound formation in the surface true solution is shifted to approximately $x_{Cu} = 0.55$ to 0.85. This is because of surface phase enrichment.

The true composition variation of the surface and bulk phases of these systems shows that the surface phase true composition is similar to that in the bulk but is enriched in the atomic element having the lower surface tension. This enrichment causes the surface true mole fraction plot to be shifted, relative to the bulk true mole fraction plot, toward the pure component having the higher surface tension. A second result is a better understanding of the relationship between the existence and position of perturbations in the surface tension isotherm and the extent of compound formation, within the framework of ICT. Thus one could in principle select metal additives that would, even in small bulk concentrations, segregate to the surface and thus tailor either the surface tension or the wetting for various applications.

Discussion and Conclusions

The STICT model achieves good quantitative representation of the surface tension isotherms of highly solvated liquid metal systems, and this success is a direct result of the careful introduction of physically meaningful parameters. Many of the previous attempts to model the surface thermodynamics of liquid metal systems could not achieve accurate agreement with the experimental data because they did not include explicitly the strong chemical interactions that are present in many of these systems. These interactions are accounted for by postulating the existence of intermetallic compounds in equilibrium with the monomers in the true solution. The number and stoichiometry of the compounds are determined by fitting the bulk activity coefficients using a bulk solution model based on ICT. The surface tensions of these compounds are then used as the parameters in the STICT model.

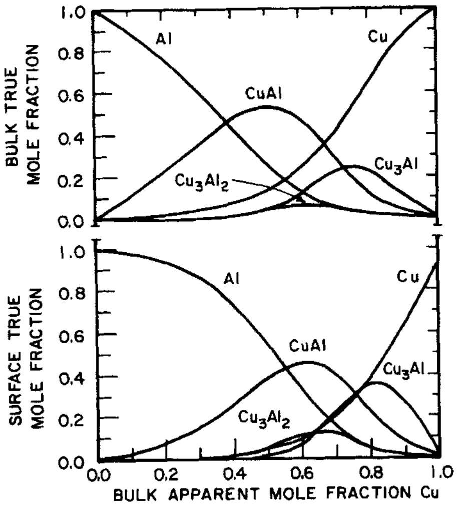

Figure 7. Bulk and surface true composition variation for Cu-Al system at 1,373 K.

The development of the STICT model is based on the Guggenheim (1952) approach; the interfacial region is pictured as a separate and homogeneous phase. The primary assumption of this work is the applicability of ideal chemical theory in determining the thermodynamic properties of this surface phase. This simplified view of the interfacial region is acceptable in modeling the surface tension of solvated liquid metal solutions. A detailed picture of the interfacial region is required if highly structure-sensitive properties are to be modeled. The modeling of experimental X-ray reflection data has been shown to be sensitive to the structure of the interfacial region (Sluis et al., 1983; Sluis and Rice, 1983).

The STICT model is very robust in that it can model a wide range of liquid metal systems. The isotherms of the systems investigated here show various types of behavior, from being nearly linear to exhibiting significant perturbations and extrema. In addition, the model can fit accurately systems that have large differences in the pure-component surface tensions. In fact, the model fit all the systems for which the necessary data were available and the assumptions of ICT are valid.

The model is quite sensitive to variations in the surface tensions of the compounds, but relatively insensitive to moderate variations in the compound molar areas (see Appendix). The latter conclusion is especially important for those systems for which excess volume data are not available, and the compound molar areas are calculated assuming zero excess volume.

A logical extension of this model would be the incorporation of physical interactions, especially for systems in which the equilibrium constants for compound formation are low or where both positive and negative deviations from Raoult's law occur. Stoicos (1982) and Alger (1982) have developed bulk phase models that include both chemical and physical interactions, and have been able to reduce the number of parameters to one chemical interaction parameter per compound, plus one physical interaction parameter, to model the bulk solution thermodynamics. Lira (1986) in reviewing these models was able to interrelate the chemical interaction parameters, thereby reducing the number of chemical interaction parameters to one, regardless of the number of compounds. This further reduces the parameters for a mixture to one physical interaction parameter and one chemical interaction parameter. Applying these results could yield a chemical-physical surface theory model able to explain and represent the behavior in a much wider class of systems.

Alger (1982) has generalized ICT for the bulk thermodynamics of multicomponent systems, assuming only that ternary or higher order intermetallic compounds are not important. An analogous extension of the STICT model to multicomponent alloy surface tensions is quite straightforward, but insufficient data exist at this time to test the result.

The STICT model assumes that the surface phase is characterized by a single monolayer. Recent computer simulation studies of the liquid-vapor interface of simple liquid metals have shown that the surface is highly stratified, exhibiting distinct atomic layers (D'Evelyn and Rice, 1983a,b; Sluis et al., 1983; Sluis and Rice, 1983; Gryko and Rice, 1984). A possible extension of the STICT model that incorporates this layering phenomenon is to treat the surface phase as a series of subphases. The thermodynamic properties of each subphase and the bulk phases can be related using the technique outlined by Eriksson (1964). The main obstacle in this approach is the description of the chemical potential for each component in each subphase.

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Notation

a – activity
A – area
K – equilibrium constant
N_{Av} – Avogardo's number
P – pressure
R – ideal gas constant
T – temperature
v – molar volume
x – apparent mole fraction
z – true mole fraction

Greek letters

α – true activity coefficient
θ – STICT model objective function
μ – chemical potential
σ – surface tension

Superscripts

b – bulk phase
calc – calculated
E – excess
exp – experimental
0 – standard state, pure component
s – surface phase

Appendix

The sensitivity of the calculated surface tension isotherm to the model parameters is an important consideration. A detailed analysis is provided in Howell (1986). For illustration we show the sensitivity of the model for a single two-compound system, Mg-Sn, chosen because it has the most complex isotherm of all the systems modeled. The long-dash curves in Figure 8 show the sensitivity of the calculated isotherm to 2% variations in the surface tensions of the compounds. The molar area sensitivity of the calculated surface tension isotherm for the Mg-Sn system is shown by the short-dash curves in Figure 8 assuming 5% variations in the area. This analysis shows that the model is quite sensitive to variations in the surface tensions of the compounds, but rather insensitive to moderate variations in the compound molar areas. The sensitivity analysis for the other six systems produces similar results.

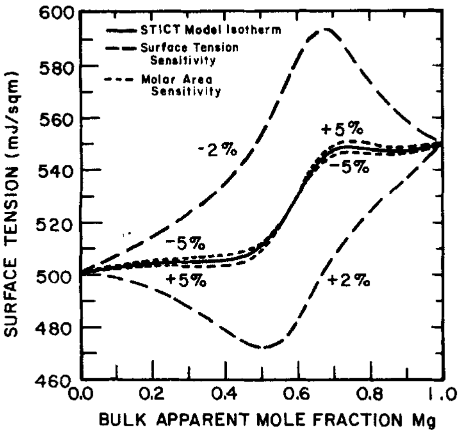

Figure 8. Sensitivity of STICT Model to variations in surface tensions and molar areas of compounds for Mg-Sn System at 1,073 K.

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