Slag-Metal Equilibrium During Submerged Arc Welding

C. S. CHAI AND T. W. EAGAR

A thermodynamic model of the equilibria existing between the slag and the weld metal during submerged arc welding is presented. As formulated, the model applies only to fused neutral fluxes containing less than 20 pct CaF_2, however some results indicate that the model may be useful in more general cases as well. The model is shown to be capable of predicting the gain or loss of both Mn and Si over a wide range of baseplate, electrode and flux compositions. At large deviations from the predicted equilibrium, the experimental results indicate considerable variability in the amount of Mn or Si transferred between the slag and metal phases, while closer to the calculated equilibrium, the extent of metal transfer becomes more predictable. The variability in metal transfer rate at large deviations from equilibrium may be explained by variations between the bulk and the surface concentrations of Mn and Si in both metal and slag phases.

SINCE its inception over forty years ago, submerged arc welding has developed into one of the most efficient, most reliable techiques of joining steel. Improvements in the flux and electrode compositions have resulted in weld metal with excellent properties. Nonetheless, the gains have been slow and have been won with considerable difficulty which is in part due to the fact that no formalism has been developed to explain the observed trends. Indeed, flux development for submerged arc and other welding processes has been approached empirically leaving a limited foundation upon which to base future progress.

A major advance in systemitizing the study of welding fluxes was begun by Christensen and Chipman[1] who investigated acidic coatings on shielded metal arc electrodes. Others following,[2-8] have made similar studies on submerged arc welding fluxes, with some success in categorizing the effects of the various flux components. Several reviews have been written upon the subject.[9,10] More recently, several theories have been proposed to explain the observed trends,[7,11-15,39] however, the conclusions are often conflicting, which leaves the field at little advantage.

An important concern of many of the previous studies has been quantification of the slag-metal reactions which occur during the welding process; however, the lack of a uniform reaction temperature and the brief reaction time results in a nonequilibrium process. The failure to achieve equilibrium presents a major difficulty in establishing a formalism for predicting the extent of these reactions. Similar difficulties occur in other slag-metal processes such as steelmaking and smelting. Much advantage has been gained in these areas through study of equilibrium thermodynamics, which is capable of defining the direction and bounds of a reaction if not the actual extent of the reaction. Attempts have been made to utilize the slag-metal equilibrium of steelmaking with respect to the welding process.[15] Unfortunately, these attempts have met with little success.

In the present paper a new formalism is developed from which to predict slag-metal equilibria during arc welding. The predicted equilibria are then compred with experimental data taken both from welding literature and from new experimental measurements. It will be shown subsequently that the new formalism is quite successful in predicting the direction and the permissable extent of both the manganese and the silicon reactions. The actual extent of the reactions is determined by kinetic factors rather than by thermodynamic factors and hence is more difficult to predict. Nonetheless the present approach is useful in establishing limits upon the chemistry changes which occur during the submerged arc welding process.

THEORETICAL APROACH

1. Initial Assumptions

As noted previously, it is a generally accepted fact that the slag and metal do not achieve equilibrium during flux shielded welding. For this reason most investigators have chosen an empirical approach to welding flux formulation. An important initial hypothesis in the present work is the belief that equilibrium thermodynamics, while unable to predict the extent of a reaction, should at least be able to predict the direction of the reaction. It is further assumed that it is possible to utilize much of the slag-metal activity data developed for steelmaking, realizing that the rate controlling reactions may be different in welding. Using these hypotheses, a model is developed which uses the following assumptions.

1) The effective temperature of chemical reactions in the weld metal pool is 2000 °C.

C. S. CHAI, presently Engineer, Lincoln Electric Co., Cleveland, OH, was formerly a Graduate Research Assistant, Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, MA 02139. T. W. EAGAR is Associate Professor of Materials Engineering, Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, MA 02139.

Manuscript submitted July 16, 1980

ISSN 0360-2141/81/0911-0539$00.75/0

2) An empirical relationship between the basicity index of the welding flux and the weld metal oxygen content is known to exist and is valid for all flux compositions of interest.

3) The activity data of steelmaking slag may be extrapolated from 1600 °C to the 2000 °C range by assuming regular solution behavior, *i.e.*, $T \ln \alpha_i$ equals a constant.

4) The primary reactions of interest are those involving silicon, manganese and oxygen.

Each of these assumptions requires some justification.

Assumption 1. In his review of welding fluxes, Jackson[9] noted that most investigators have measured the maximum weld pool temperature as 2000 °C using thermocouple techniques. This temperature is an average value representing the median between the fusion temperature (approximately 1500 °C) and the weld pool surface temperature in the arc vicinity, which may be roughly estimated from metal evaporation data as 2500 °C.* It should also be noted that Christensen and Chipman[1] and Belton *et al*[3] found an effective equilibrium temperature for the MnO and the SiO_2 reactions respectively in selected fluxes, to be 2000 °C based upon chemical analysis of the weld metal.

Perhaps more important than either of these justifications is the finding which will be presented subsequently that equilibria based upon 2000 °C agree with the experimental data while equilibria based upon other temperatures do not.

Assumption 2. Kubli and Sharav[2] showed that the oxygen content of submerged arc weld metal decreases with increasing flux basicity. Tuliani *et al*,[18] quantified the oxygen content of the weld metal as a function of the basicity index. The International Institute of Welding flux basicity index (BI) used by Tuliani *et al* is given by:

$$BI = \frac{CaF_2 + CaO + MgO + BaO + SrO + Na_2O + K_2O + Li_2O + 1/2(MnO + FeO)}{SiO_2 + 1/2(Al_2O_3 + TiO_2 + ZrO_2)} \qquad [1]$$

Eagar[13] has modified this relationship slightly by omitting the CaF_2 term. The relationship between the weld metal oxygen content and the welding flux basicity, based upon Tuliani's data and Eagar's BI is shown in Fig. 1. Much more data could be added to this graph, however, the trend would not be changed. The oxygen content of welds produced with acid fluxes has been found experimentally to be strongly dependent upon the BI of the flux while the oxygen content of basic fluxes is essentially independent of the BI. An explanation for this trend has been given by Eagar.[13,14]

In the model presented here, the oxygen content of a given flux is estimated *a priori* from the solid line of Fig. 1.

Assumption 3. No experimental justification of this assumption is available. This hypothesis is made as a matter of convenience due to lack of any better alternative. However it should be noted that the slag acitivites are changed relatively little by this assumption. For example, the activity of SiO_2 in a 40 pct CaO-60 pct SiO_2 melt is changed from 0.80 at 1600 °C to 0.75 at 2000 °C by assuming regular solution behavior.

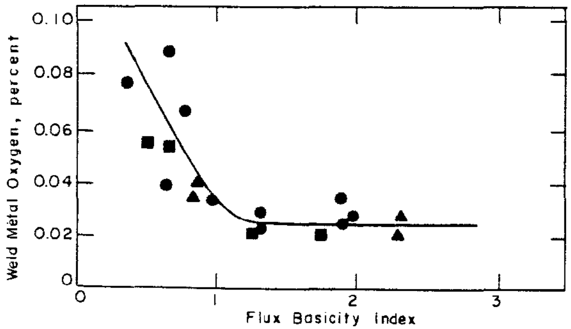

Fig. 1—The empirical relationship between the weld metal oxygen and the flux basicity index when using the submerged arc welding process. (After Tuliani, *et al* [18])

Assumption 4. The oxidizing potential of welding fluxes is not controlled by the FeO content of the slag as it is in ironmaking and steelmaking. Although fluxes high in FeO produce large weld metal oxygen contents,[1] the oxygen content of welds made with fluxes containing less than ten percent FeO is not noticeably influenced by the FeO content of the flux.[3,18] Eagar has shown that this may be due to the formation of suboxides at the higher temperatures involved in welding.[14] In any case, almost all commercial submerged arc welding fluxes have very low FeO contents--typically less than two percent.

North has claimed that CaO in the flux contributes oxygen to the weld metal,[7] however, his fluxes were made of blended minerals in which he used $CaCO_3$ as a source of CaO. It is likely that the increasing oxygen content with increasing CaO in North's fluxes is due to carbonate decomposition and not CaO decomposition as he concluded. In any case, little calcium is found in the weld metal which confirms the fact that the calcium reaction is relatively unimportant in welding.

Although free aluminum or free titanium in the baseplate or welding electrode certainly reacts with the oxygen in the weld metal, the quantity of these strongly deoxidizing elements is generally low in carbon and low alloy steels. Most welding experiments indicate that little or none of these elements is recovered in the weld metal, but that these elements are entirely consumed in either the flux or as inclusions in the weld metal. Similar arguments may be made for the other cations of the typical flux components listed in Eq. [1].

The carbon-carbon monoxide reaction is important as oxidation of carbon does increase the weld metal

---

*This estimate is obtained by equating the heat lost by metal evaporation as calculated by Cobine and Burger[16] to the heat transferred to the weld pool surface as measured by Nestor.[17]

deoxidation rate, and hence influences the recovery of Mn and Si; however, the work of Christensen[32] shows that the changes in Mn and Si are generally much greater than the change in weld metal carbon content. On this basis, the most important, but by no means the only slag-metal reactions are those involving Mn and Si.

Using the above assumptions, it is possible to formulate a model of the thermodynamic equilibrium which should prevail in flux shielded arc welding. An outline of the calculation procedure follows.

2. Calculation Procedure

Belton *et al*[3] have derived the following thermodynamic data for the SiO_2 reaction in the temperature range 1713 to 2000 °C.

$$SiO_{2(l)} = \underline{Si} + 2\underline{O}$$

$$\log K = \frac{-28360}{T} + 10.61$$

$$K = \frac{a_{Si}a_O^2}{a_{SiO_2}} \qquad [2]$$

where the standard state for SiO_2 in the slag is pure SiO_2 and the standard state for oxygen and silicon in the weld metal is based upon a 1 pct solution.

Table I. Slag Systems and Temperatures for Which Thermodynamic Activity Data are Available

System	Temperature(°C)	Reference
$MnO-SiO_2$	1500–1600	28
$CaO-SiO_2$	1500–2050	3
$MnO-CaO-Al_2O_3$	1560	29
$CaO-MnO-SiO_2$	1650	28
$FeO-MnO-SiO_2$	1560	30
$FeO-MnO-Al_2O_3$	1560	31
$CaO-Al_2O_3$	1700	28
$SiO_2-MgO-Al_2O_3$	1600	32
$SiO_2-CaO-MgO$	1600	32
$CaO-FeO-SiO_2$	1550	32
$FeO-MnO-TiO_2$	1475	33
$MnO-TiO_2-SiO_2$	1500	33
$SiO_2-CaO-Al_2O_3$	1600	32
$MnO-CaO-Al_2O_3-SiO_2$	1650	34

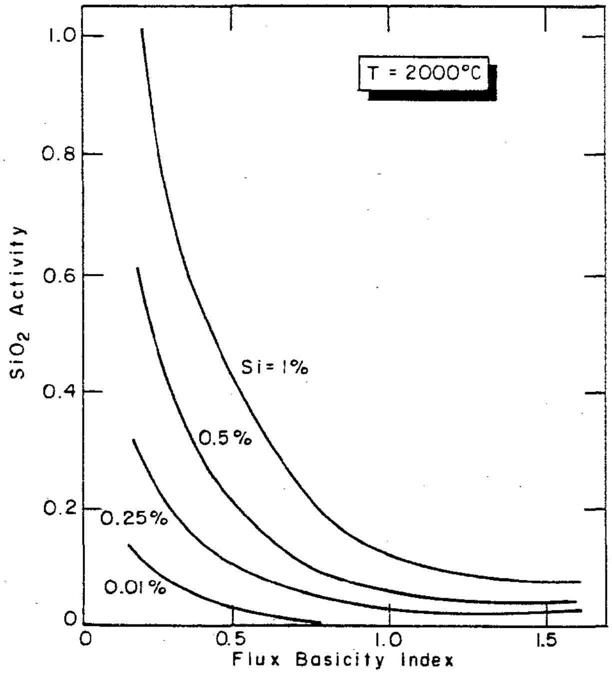

Fig. 2—The relationship between the activity of SiO_2 and the flux basicity index for a given weld metal Si content at 2000 °C assuming regular solution behavior in the flux.

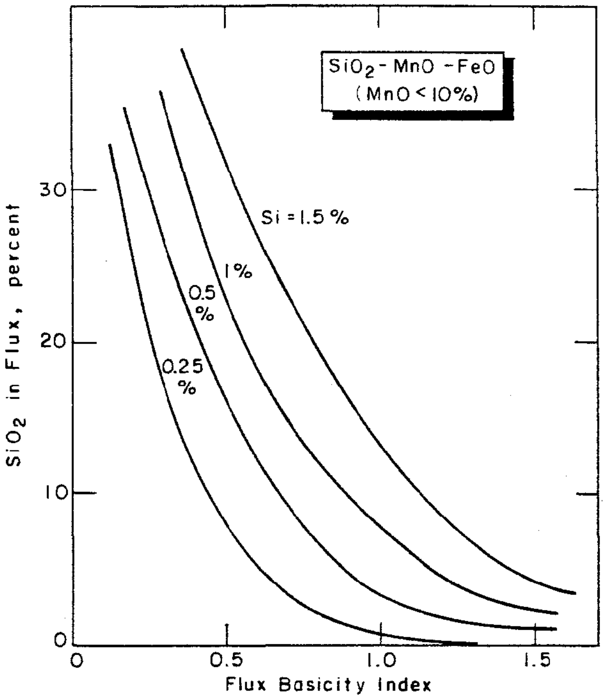

Fig. 3—The relationship between the equilibrium percent SiO_2 and the flux basicity index for a given weld metal Si content in the SiO_2-MnO-FeO system at 2000 °C.

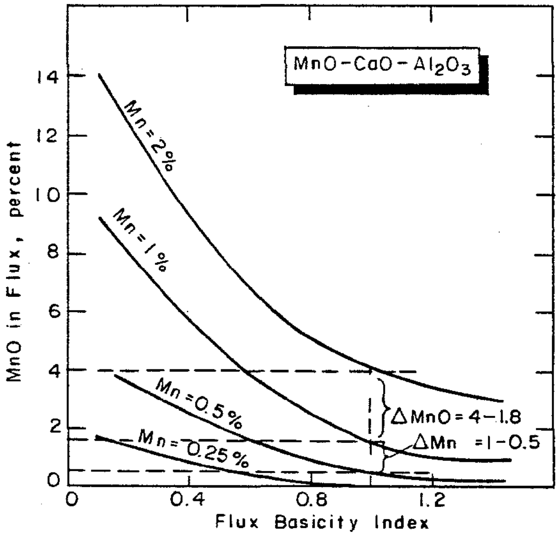

Fig. 4—The relationship between equilibrium percent MnO and the flux basicity index for a given weld metal Mn content in the $MnO-CaO-Al_2O_3$ system at 2000 °C. The dotted lines are presented for reference to discussion in the text.

Using Assumption 1 and neglecting interaction terms gives the relationship

$$\alpha_{SiO_2} = 73.6\ (\text{wt/pct } \underline{Si})\ (\text{wt/pct } \underline{O})^2 \qquad [3]$$

Upon application of Assumption 2 and Eq. [3], the data of Fig. 2 may be obtained. Using Assumption 3, and available activity data for several flux systems given in Table I, data such as Fig. 3 may be calculated.

A similar procedure may be used for the manganese reaction beginning with

$$\underline{Mn} + \underline{O} = MnO_{(l)}$$

$$\log K = \frac{12760}{T} - 5.68$$

$$K = \frac{\alpha_{MnO}}{\alpha_{Mn}\alpha_O} \qquad [4]$$

The manganese equation analogous to Eq.[3] is

$$\alpha_{MnO} = 0.86\ (\text{wt/pct } \underline{Mn})\ (\text{wt/pct } \underline{O}) \qquad [5]$$

Assumptions 2 and 3 again give a relationship for a specific flux system of the type shown in Fig. 4.

Figures 3 and 4 represent the predicted equilibrium between the Si or Mn in the weld metal and the SiO_2 or MnO in the slag respectively, as a function of the basicity index of the flux.*

The equilibria also vary with the flux system. A listing of flux systems for which sufficient activity data are available is given in Table I.

EXPERIMENTAL VERIFICATION OF THE THEORY

Experimental verification of the proposed theoretical equilibria is necessary if only because the assumptions themselves are not easily verifiable. The value of any theory is in proportion to its ability to provide accurate predictions of the parameters of interest. To this end two separate verification techniques were used.

In the first, slag-metal reaction data available from the literature were used to determine if the theory is capable of predicting the trend of Mn and Si transfer for a wide range of flux, electrode and baseplate compositions. This test is thought to demonstrate the generality of the theory.

In the second, the accuracy of the theory was investigated by meaurement of the extent of Mn and Si transfer as a function of the electrode/baseplate composition. This test measures the ability of the theory to predict the specific equilibrium compositions. As will be shown subsequently, the theory withstood each of these tests with remarkable success.

1. Verification of the Generality of the Theory

Consider the equilibria described by Fig. 3 and 4. These apply specifically only to SiO_2-MnO-FeO and MnO-CaO-Al_2O_3 fluxes; however, equilibria of a similar nature may be generated for each of the flux systems shown in Table I. It should be noted that the marked dependence of equilibrium MnO or SiO_2 content as a function of the flux BI is general, *i.e.*, one always finds the equilibrium flux composition to be strongly dependent upon the flux BI. As such, minor errors in determining the flux BI should produce large errors in the equilibrium prediciton.

As an example, consider a flux of composition 31 pct CaO-4 pct MnO-65 pct Al_2O_3. The BI as given by Eq. [1] is one. If a baseplate and electrode with average initial composition 0.5 pct Mn is used for welding, the equilibria of Fig. 4 would predict an equilibrium weld metal content of 2 pct Mn. If the theory is correct one would expect the weld metal to gain Mn by decomposition of part of the MnO in the slag during welding. Fortunately, the slag BI does not differ appreciably from that of the flux,[18] so that an iterative procedure is not required. The final weld metal Mn content is expected to lie between 0.5 pct and 2.0 pct. We may define two quantitites, *viz*,

$$\Delta Mn = Mn_f - Mn_i \qquad [6]$$

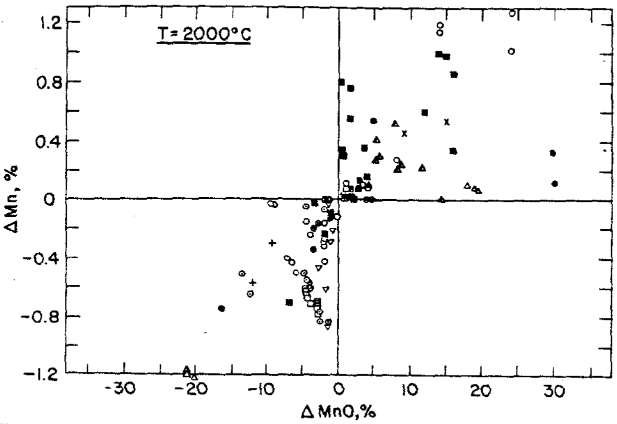

Fig. 5—Variation of change in weld metal manganese, ΔMn, with deviation of flux MnO from predicted equilibrium, ΔMnO. Note that all data points lie within the first and third quadrants.

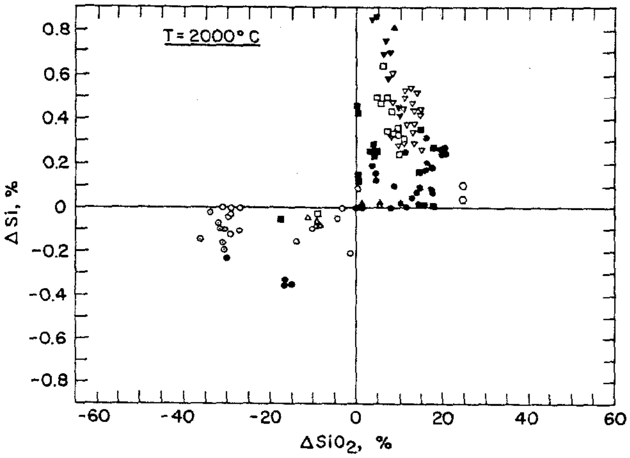

Fig. 6—Variation of change in weld metal silicon, ΔSi, with deviation of flux SiO_2 from predicted equilibrium ΔSiO_2. Note that all data points lie within the first and third quadrants.

---

* In this paper, flux is used to describe the starting material prior to welding while slag denotes the molten or fused flux during or after welding.

and

$$\Delta MnO = MnO_i - MnO_{f,eq}. \qquad [7]$$

Where Mn_f is the measured final weld metal manganese content, Mn_i is the average initial electrode/baseplate manganese content, MnO_i is the initial flux MnO content, and $MnO_{f,eq}$ is the percent MnO in the slag which would be in equilibrium with the final weld metal manganese as predicted by Fig. 4.

If in the example given $Mn_f = 1.0$ pct, then $\Delta Mn = 1.0 - 0.5 = 0.5$ pct and from Fig. 4 we find $\Delta MnO = 4.0 - 1.8 = 2.2$ pct. ΔMnO is a measure of the deviation from equilibrium and may be considered as a stimulus while ΔMn is the response to this stimulus. If the initial flux contains an excess of MnO with respect to the initial flux basicity and electrode/baseplate equilibrium, MnO from the slag will decompose thereby increasing the weld metal Mn content. The larger the initial MnO deviation from the final predicted equilibriuim value, the greater is the stimulus for MnO decomposition. As noted above, ΔMn is a measure of the response to this stimulus. Reversing the order of the initial-final subscripts between Eq. [6] and [7], ensures that a positive stimulus will produce a positive response and conversely a negative stimulus will provide a negative response. In a physical sense, Eqs. [6] and [7] are written such that a loss of manganese from the slag as predicted by the theory (positive) will result in a gain of manganese in the weld metal (also positive). If a positive stimulus should produce a negative response, or vice versa, the equilibrium predicition of the theory would be in error.

Such tests of the theory may be made if one has the following information:

a) The initial flux composition. Equation [1] is then used to calculate a BI. To a very good approximation the slag BI is assumed to be the same as the flux BI.[18] MnO_i is determined from the flux composition.

b) The initial electrode and baseplate chemistries and the final weld metal analysis and dilution. If the dilution is not given, it may be assumed to be 0.5 for most submerged arc welds.[19] Mn_i and Mn_f are taken directly from these analyses. $MnO_{f,eq}$ is obtained from an equilibrium plot such as Fig. 4.

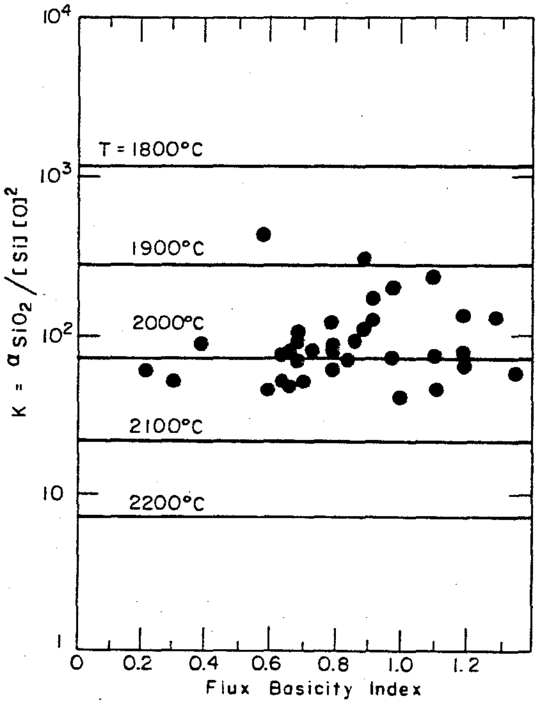

Fig. 7—The effective weld pool temperature as measured by the SiO_2 reaction equilibrium constant.

The analysis described above has been performed for over one hundred welds as reported in the literature.[3,5,7,8,18,20-27] The data represent a wide range of welding conditions with flux basicities varying from 0.2 to 4.0, and initial manganese and silicon contents varying from 0.01 to 3.1 pct and 0.002 to 1.0 pct respectively. Most welding fluxes were commercial formultions containing seven or more components. Since the available thermodynamic data is generally only available for ternary or quarternary formulations (*Cf*. Table I), only equilibria from flux systems comprising at least 80 pct of the commerical flux compositional anlysis were compared. This tends to exclude welding fluxes with greater than 15 to 20 pct CaF_2 although the analysis has been found to work reasonably well with these fluxes as well.[28].

The results of the analysis of these welds are shown in Fig. 5 and 6 for manganese and silicon respectively. It

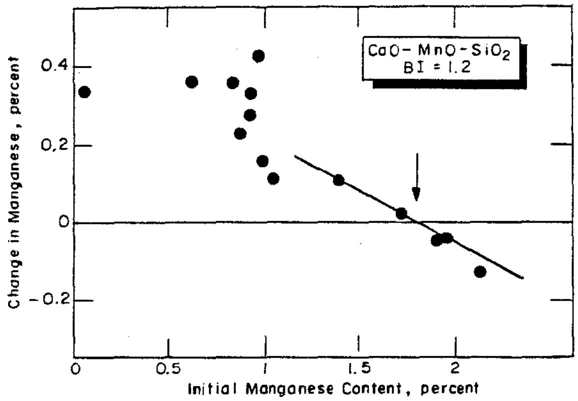

Fig. 8—The change in weld metal manganese content ΔMn, as a function of the initial manganese content measured with a CaO-MnO-SiO_2 flux using the artificial baseplate technique. The arrow denotes the predicted equilibrium manganese content for this flux system.

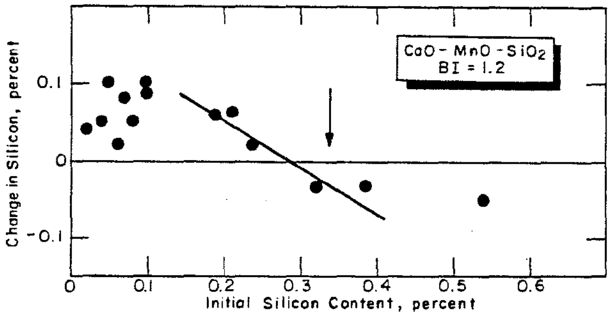

Fig. 9—The change in weld metal silicon content, ΔSi, as a function of the initial silicon content measured with a CaO-MnO-SiO_2 flux using the artificial baseplate technique. The arrow denotes the predicted equilibrium silicon content for this flux system.

Table II. Comparison of Theoretically Predicted Mn and Si Equilibrium with the Values Measured Experimentally

Flux Designation Type	Flux Basicity Index	Predicted Mn, Pct	Measured Mn, Pct	Predicted Si Pct	Measured Pct	Reference
F-1 $CaO-MnO-SiO_2$	1.17	1.83	1.85	0.33	0.28	This work
F-2 $CaO-MnO-SiO_2-Al_2O_3$	0.5	0.4	0.44	0.25	0.29	This work
F-3 $MnO-SiO_2$	0.46	1.1	1.27	0.80	0.95	This work
F-4 $CaO-SiO_2$	1.45	0	<0.5	0.32	0.25	This work
MIT-1 Al_2O_3	0.52	0.2	0.15	0.15	0.25	This work
MIT-2 $CaO-SiO_2$	0.52	0	<0.32	1.3	>1.18	This work
LW280 $CaO-Al_2O_3-SiO_2$	0.85	1.25	1.25	0.5	$\simeq 0.7$	39
F-a $CaO-SiO_2-Al_2O_3$	0.81	0	0.1	1.6	n.d.	5
F-c $CaO-SiO_2-Al_2O_3$	0.45	0	0.1	1.0	n.d.	5
F-d $CaO-SiO_2-Al_2O_3$	0.53	0	0.2	1.3	n.d.	5
F-e $CaO-MnO-SiO_2$	0.63	1.75	1.55	n.d.	n.d.	5
F-f $CaO-MnO-SiO_2$	1.02	0.38	0.56	0.5	n.d.	5

n.d.--not determined.
All fluxes except F-1, F-2, MIT-1 and MIT-2 are commercial compositions.

Table III. Comparison of Effective Reaction Temperature of Manganese Based Upon Slag/Metal Surface Chemistries and Bulk Chemistries

Test Number	Initial Manganese Mn,*i*, Pct	Final Surface Manganese Mn,*s*, Pct	Final Bulk Manganese Mn,*b*, Pct	Final Bulk Oxygen O,*b*, pct	Surface Equilibrium Temperature T_s,°C	Bulk Equilibrium Temperature T_b,°C
1	1.85	1.85	1.85	0.050	1979	1979
2	1.40	1.85	1.50	0.047	1968	1932
3	0.09	0.82	0.48	0.068	1896	1812
4	1.74	1.75	1.75	0.072	2031	2031
5	1.00	1.50	1.15	0.052	1950	1905
6	0.85	1.62	1.20	0.062	1992	1941
7	0.07	1.50	0.40	0.035	1885	1694
8	0.94	—	1.27	0.030	—	1835
9	0.98	—	1.40	0.049	—	1928
10	0.64	—	1.00	0.060	—	1906
11	1.95	1.90	1.90	0.046	1968	1968
12	0.88	1.50	1.10	0.056	1962	1910
13	1.15	0.36	0.64	0.086	2050	2164
14	1.26	0.36	0.56	0.077	2031	2115
15	1.08	0.33	0.55	0.068	1994	2088
16	1.10	0.53	0.65	0.084	2119	2158
17	1.01	0.39	0.69	0.071	2031	2138
18	1.11	0.29	0.57	0.053	1929	2047
19	1.25	0.44	0.60	0.063	2031	2088
20	0.96	0.39	0.60	0.090	2074	2158

Tests 1 through 12 from this study.
Tests 13 through 20 from Christensen (Ref. 5)
Note the wider variation in reaction temperature when using bulk chemical analysis.

will be noted that none of the data falls within either the II or IV quadrants. This confirms that the stimulus predicted by the equilibrium theory agrees with the response as determined experimentally. Considering the imprecision with which one knows the actual weld metal chemistry as well as the imprecision of the thermodynamic data, the agreement of the theory and experiment is quite remarkable.

It is worthy of note, that a similar analysis using thermodynamic data based upon 1800 °C would not yield good agreement, while an analysis based upon an equilibrium temperature of 2200 °C, compresses the data so as to obscure any trends. In addition, weld metal equilibrium reaction temperatures based upon the SiO_2 reaction (Eq. [2]) agree with the 2000 °C assumption as may be seen in Fig. 7. Several of the welds of Fig. 7 were preoduced with 3 pct silicon iron baseplate, using very high basicity (low silica activity) fluxes. In such a case one would expect transport of a large amount of silicon from the weld pool to the slag. The finding that the weld/slag equilibrium remains at 2000 °C suggests that silicon transport is very rapid during submerged arc welding. The data confirm the finding of Belton *et al*[3] that the SiO_2 reaction achieves an effective equilibrium reaction temperature of 2000 °C over a wide range of weld metal chemistry and flux composition.

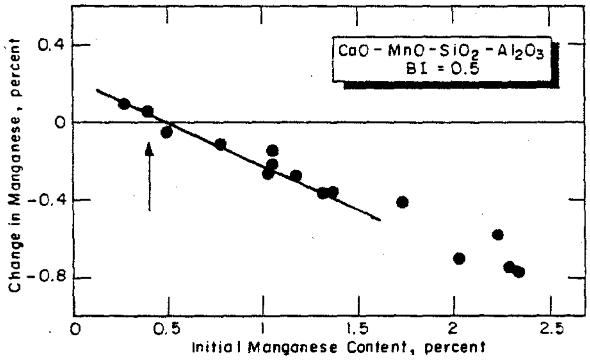

Fig. 10—The change in the weld metal manganese content, ΔMn, as a function of the initial manganese content measured with a CaO-MnO-SiO_2-Al_2O_3 flux using the artificial baseplate technique. The arrow denotes the predicted equilibrium manganese content for this flux system.

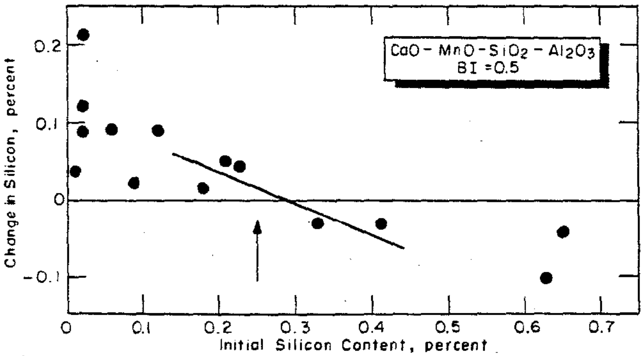

Fig. 11—The change in weld metal silicon content, ΔSi, as a function of the initial silicon content measured with a CaO-MnO-SiO_2-Al_2O_3 flux using the artificial baseplate technique. The arrow denotes the predicted equilibrium silicon content for this flux system.

2. Verification of the Accuracy of the Equilibrium Mn and Si Predicitions

Although the previous test confirms the generality of the theory, it does not prove the accuracy of the predictions. Indeed, there is considerable scatter of the data within quadrants I and III of Figs. 5 and 6. This scatter may be explained in part by the nonequilibrium nature of slag-metal reactions in welding.[29] Nonetheless, it is of interest to determine the accuracy with which the theory can predict not only the gain or loss of Mn or Si from the weld pool, but also the composition at which change in composition is expected to be zero.

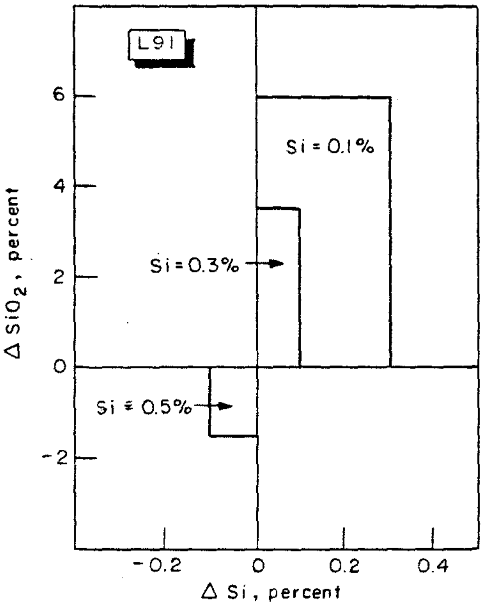

Fig. 12—The predicted reltionship between ΔSi and ΔSiO_2 for commercial flux L91. The prediciton indicates little possible change in weld silicon content for initial values between 0.3 and 0.5 pct silicon.

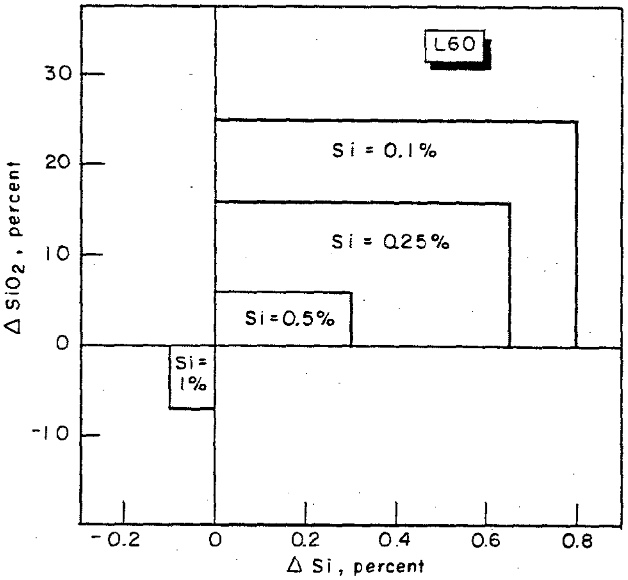

Fig. 13—The predicted relationship between ΔSi and ΔSiO_2 for commercial flux L60. Most baseplates and electrodes contain less than 0.5 pct silicon which would be increased by use of this flux.

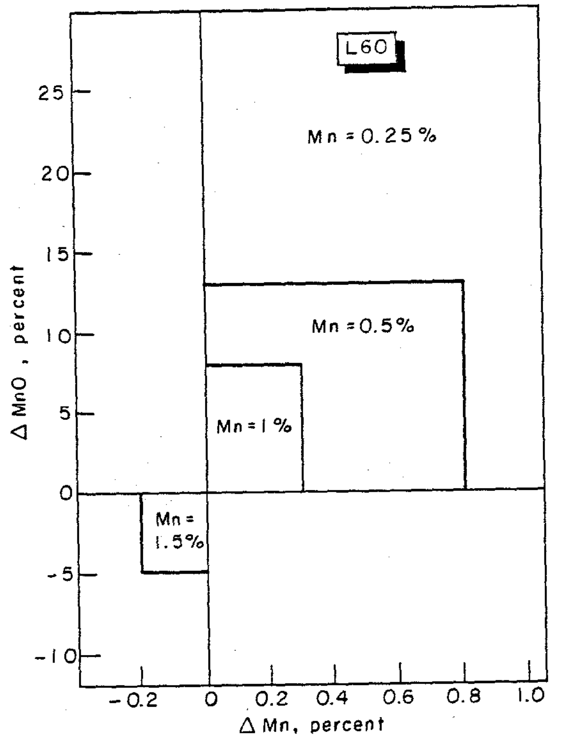

Fig. 14—The predicated relationship between ΔMn and ΔMnO for commercial flux L60.

Several authors have attempted to study slag-metal reactions during welding by producing a pyramid of weld beads, of which each succeeding layer is diluted by a smaller fraction of the base metal.[1,5,8,39] In this way, it is claimed that the final flux/electrode 'equilibrium' may be attained. This is not necessarily true; the pyramid of weld beads leads to a steady state weld metal composition rather than an equilibrium composition. This is caused by the continuous disruption of the weld pool chemistry by the melting electrode. Only if the elecrode is of a composition which corresponds to equilibrium with the flux will metal transfer between the weld pool and the slag be zero. In all other cases, the transfer reaches a steady state which is a balance between the rate of the slag-metal reaction and the rate of weld pool dilution caused by the melting electrode.

In order to overcome the difficulties with the pyramid bead test, it is desirable to have an electrode and a baseplate of identical composition; hence, dilution effects may be neglected. Such identical electrode/baseplate compositions are very difficult to obtain. Instead, we have chosen to create an artificial baseplate by bundling seven or eight lengths of electrode and placing these on a water cooled copper hearth. in this way, 'welds' may be made with an electrode and baseplate of identical composition. A series of welds is made, varying the Mn or the Si content of the electrode until a given flux produces no net change in the deposit chemistry as compared with the electrode chemistry. This composition represents the composition of Mn or Si in equilibrium with the flux. In practice it is convenient to vary either the Mn or the Si content without attempting to hold the composition of the other element constant. Although this ignores interaction effects between the Mn and Si recoveries, it was found to be a useful aproach. An example of two such series of tests are given in Figs. 8 through 11. It is seen that the Mn or the Si content in the weld deposit may vary unpredictably when the electrode deviates significantly from the equilibrium content but that the variation is much more consistent near the equilibrium concentration. The arrows in Figs. 8 through 11 indicate the predicted equilibria as obtained from graphs similar to Figs. 3 and 4. Table II gives the measured and the predicted equilibria for similar such tests made in our laboratory and by others. It is seen that the agreement is generally quite good, hence the accuracy of the predicted equilibria is judged to be acceptable.

DISCUSSION

The above theory provides a means of calculating the weld metal Mn or Si content which is in equilibrium with a flux of a known composition. As such the theory has been shown to be capable of predicting the direction, if not the magnitude, of the change in these elements during welding.

Furthermore, the artificial baseplate experiments indicate that the approach to equilibrium is well behaved for small deviations from the equilibrium but varies considerably as one elects an electrode/baseplate composition which does not correspond closely to equilibrium with the flux. Recent results from our laboratory indicate that the larger deviations from equilibrium result in nonuniform distributions of Mn and sometimes of Si in the weld metal and of MnO and SiO_2 in the slag. The distribution in the slag phase may be markedly nonuniform; hence, the use of bulk composition values may lead to erroneous predictions in terms of quantifying the extent of the Mn or the Si changes. When one uses the surface compositions rather than the bulk compositions of Mn and Si in the metal and slag phases, the predictions correspond more closely to a reaction temperature equilibrium of 2000 °C. Several examples of the predicted equilibrium reaction temperatures based upon the bulk and the surface compositions of Mn are given in Table III. It may be seen that the temperatures based upon the surface compositions are more uniform and are centered about an effective reaction temperature of 2000 °C. This provides a further justification for assumption 1.

As presented the analysis applies only to fused, neutral submerged arc welding fluxes with CaF_2 content of less than 20 pct* although several tests indicate that the approach may be applicable to fluxes with higher CaF_2 contents as well. Comparison of the predictions with the results of other flux shielded welding processes would be welcomed. Extension of the experimental work to blended submerged arc fluxes is underway in our laboratory. The preliminary results are encouraging that the techique may be useful for these systems as well. If successful, this work, coupled with a mass balance formalism, will hopefully provide a means of

---

*The restriction to systems with less than 20 pct CaF_2 is based upon the limited activity data for CaF_2-metal oxide slags.

predicting Mn and Si transfer in active submerged arc fluxes.

Although the study as presented is only approximate, and has been verified using *a posteriori* data, it may be of use in selecting combinations of flux/electrode/baseplate *a priori*. Consider for instance, the predicted equilibria of Fig.12 through 14, which represent two commercial fluxes. The predicted equilibrium silicon content for flux L91 is approximately 0.4 pct Si. Electrode/baseplate combinations below this value should gain silicon in the weld metal when this flux is used, while values greater than 0.4 pct would lead to loss of silicon during welding. The initial MnO in flux L91 is essentially zero suggesting that this flux would always lead to loss of manganese from the weld pool. Flux L60 would be relatively inert when using an electrode/baseplate of average composition 1.27 pct Mn and 0.85 pct Si. While these graphs do not predict the exact composition of the weld metal to be deposited, they may be used to predict the permissable variations. Although in many cases these variations are quite wide, in other cases, the predicted range restricts the possible weld metal compositions considerably. It is anticipated that these more restrictive flux/electrode/baseplate compositions may perform more reproducibly in practice.

SUMMARY

A theory predicting slag-metal equilibrium during submerged arc welding with fused neutral fluxes has been presented. Although not capable of predicting the magnitude of the Mn and Si changes in the weld metal, the theory is capable of predicting the gain or loss of these elements over a wide range of flux/electrode/baseplate compositions. As such, it represents a significant advance in our ability to predict and control the extent of these reactions. Further studies relating this work to other types of submerged arc welding fluxes and other welding processes is desirable.

ACKNOWLEDGMENTS

The authors gratefully acknowledge support for this study from the National Science Foundation under grant DMR77-27230. They are also grateful to Dr. Harry Bishop of Allegheny-Ludlum Steel Corporation for supplying the three percent silicon iron plate used for several of the trials.

REFERENCES

1. N. Christensen and J. Chipman: *Weld. Res. Counc. Bull.*, January 1953, no. 15.
2. R. A. Kubli and W. B. Sharav: *Weld. J.*, 1961, vol. 40, no. 11, p. 497-s.
3. G. R. Belton, T. J. Moore, and E. S. Tankins: *Weld. J.*, 1963, vol. 42, no. 7, p. 289-s.
4. W. J. Lewis and P. J. Rieppel: *Weld. J.*, 1961, vol. 40, no. 8, p. 337-s.
5. N. Christensen: Report AD-602138, NTIS, Arlington, VA, November, 1965.
6. C. A. Butler and C. E. Jackson: *Weld. J.*, 1967, vol. 46, p. 448-s.
7. T. H. North, H. B. Bell, A. Nowicki, and I. Craig: *Weld. J.*, 1978, vol. 57, no. 3, p. 63-s.
8. T. H. North: *Weld. Res. Abroad*, January 1977, vol. 23, no. 1, p. 2.
9. C. E. Jackson: *Weld. Res.Counc.*, December 1973, no. 190.
10. J. G. Garland and N. Bailey: M/84/75 The Welding Institute, Abington, England, 1975.
11. J. H. Palm: *Weld. J.*, 1972, vol. 51, no. 7, p. 358-s.
12. T. Boniszewski: *Met. Const. Br. Weld. J.*, 1974, vol. 6, p. 128.
13. T. W. Eagar: *Weld. J.*, 1978, vol. 57, no. 3, p. 76-s.
14. T. W. Eagar: *Weldments: Physical Metallurgy and Failure Phenomena*, R. J. Christofel, E. F. Nippes, and H. D. Solomon, eds., p. 31, General Electric Co., Schenectady, NY, 1979.
15. B. A. Korh: *Autom. Weld.*, 1977, vol. 30, no. 7, p. 16.
16. J. D. Cobine and E. D. Burger: *J. Appl. Phys.*, 1955, vol. 26, no. 7, p. 895.
17. O. H. Nestor: *J. Appl. Phys.*, 1962, vol. 33, no. 5, p. 1638.
18. S. S. Tuliani, T. Boniszewski, and N. F. Eaton: *Weld. Met. Fabr.*, 1969, vol. 37, no 8, p. 327.
19. B. G. Renwick and B. M. Patchett: *Weld. J.*, 1976, vol. 55, no. 3, p. 69-s.
20. J. G. Garland and P. R. Kirkwood: *Welding of Line Pipe Steels*, K. H. Koopman, ed., p. 176, Welding Research Council, New York, 1977.
21. S. F. Baumann, J. R. Sawhill, and M. Nakabayashi: *ibid*, p. 56.
22. W. K. C. Jones: *Weld. J.*, 1976, vol. 55, no. 2, p. 42-s.
23. A. P. Bennett and P. J. Stanley: *Br. Weld. J.*, 1966, vol. 13, no. 2, p. 59.
24. G. Uttrachi: private communication, Union Carbide Corp., Astabula, OH, 1977.
25. J. G. Garland and P. R. Kirkwood: *Weld. Met. Fabr.*, 1976, vol. 44, no. 4, p. 217.
26. N. Bailey: *Weld. Res. Int.*, 1978, vol. 8, no. 3, p. 215.
27. J. G. Garland and N. Bailey: *ibid*, 1978, p. 240.
28. C. S. Chai and T.W. Eagar: unpublished research, MIT, Cambridge, MA, 1977.
29. C. S. Chai and T. W. Eagar: *Weld. J.*, 1980, vol. 59, no. 3, p. 93-s.
30. J. F. Elliott, M. Gleiser, and V. Ramakrisna: *Thermochemistry for Steelmaking*, Vol. II, Addison Wesley Publishing Co., Reading, MA, 1963.
31. F. D. Richardson: *Physical Chemistry of Melts in Metallurgy*, Vol. I, Academic Press, NY 1974.
32. N. Christensen: *Jernkontorets Ann.*, 1977, vol. JkA-77, no. 5, p. 4.
33. H. Fujita and S. Maruhaski: *Tetsu To Hagane*, 1970, vol. 56, p. 830.
34. S. Maruhashi: *Tetsu To Hagane*, 1971, vol. 57, p. 891.
35. R. H. Rein and J. Chipman: *Trans. TMS-AIME*, 1965, vol. 233, p. 415.
36. E. Martin, O. I. H. Abdelkarim, I. D. Somerville, and H. B. Bell: *Metal-Slag-Gas Reactions and Processes*, Z. A. Foroulis and W. W. Smeltzer, eds., p. 1, The Electrochemical Society, Princeton, NJ, 1975.
37. *The Making, Shaping and Treating of Steel*, H. E. McGannon, ed., 9th ed., U.S. Steel, 1971.
38. J. G. Garland and P. R. Kirkwood: *Met. Constr.*, 1975, vol. 7, no. 6, p. 320.
39. H. Thier: *Proceedings of the Conference on Weld Pool Chemistry and Metallurgy*, p. 271, The Welding Institute, London, April 1980.