

Slag Metal Reactions during Submerged Arc Welding of Alloy Steels

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The transfer of Cr, Si, Mn, P, S, C, Ni, and Mo between the slag and the weld pool has been studied for submerged arc welds made with calcium silicate and manganese silicate fluxes. The results show a strong interaction between Cr and Si transfer but no interaction with Mn. The manganese silicate flux produces lower residual sulfur while the calcium silicate fluxes are more effective for removal of phosphorus. The effective oxygen reaction temperature lies between 1700 and 2000 °C for all elements studied. Evidence of Cr and Mn loss by metal vaporization is also presented.

I. INTRODUCTION

DURING the past two decades there has been tremendous progress in steel technology leading to many alloys possessing excellent mechanical and corrosion resistant properties. In many cases it is necessary to join these materials by welding techniques which are capable of achieving similar properties.

Recently much work has been done on slag-metal reactions of submerged arc welds involving manganese, silicon, and oxygen transfer.¹⁻⁴ This work has resulted in a better understanding of the basic and semi-basic fluxes which are capable of achieving excellent properties in carbon and low alloy steels. Much less work has been done on the reactions during submerged arc welding involving chromium, molybdenum, and nickel steels, although low and high alloy steels with these elements are finding increased use in energy conversion technologies. Also, research on slag-metal reactions of alloy steels has generally been confined to either the austenitic stainless steels^{5,6} or to steels containing less than 2.5 pct chromium.^{7,8}

The objective of the present investigation was to determine the extent of the interaction between slags and weld metals containing chromium, molybdenum, and nickel in addition to carbon, silicon, manganese, sulfur, and phosphorus. This study utilizes the concept of an equilibrium or neutral point as developed by Chai¹ and provides an estimate of the effective reaction temperature between the slag and the metal. In addition, the spatial distribution of chro-

mium, silicon, and manganese in the weld metal has also been investigated.

II. EXPERIMENTAL PROCEDURE

The experiment consisted of producing undiluted weld beads by using electrodes and baseplates of the same composition. Other researchers^{2,3} have used multiple bead pad techniques to study slag-metal equilibrium, but this method gives only a steady state weld metal chemistry. Since it is difficult to procure alloy steel baseplates and electrodes of identical chemical composition, artificial baseplates were made from the wire electrodes. Fifteen to eighteen pieces approximately 0.6 m long were cut from each electrode spool, straightened, and tied together to produce the artificial baseplate. This was then placed on a water cooled copper trough and welded using an identical electrode. During the experiment the welding parameters were kept constant with the voltage at 30 V DCEP, welding current at 350 A, and travel speed at 6.16 mm per second. Throughout the experiment it was necessary to maintain these constant welding conditions since varying welding parameters can appreciably change weld metal chemical composition unless one is operating precisely at the neutral point.^{1,9}

Seven alloy steel electrodes with chromium content varying from 1.37 to 26.31 pct were used. The chemical composition of these electrodes is shown in Table I. Four fluxes were used, the chemical composition of which is shown

Table I. Chemical Composition of Electrodes Used

Electrode	Pct Cr	Pct C	Pct Mn	Pct Mo	Pct Ni	Pct O	Pct S	Pct Si
5151	1.37	0.220	0.51	0.52	0.10	0.046	0.021	0.23
5212	2.38	0.103	0.52	0.97	0.05	0.043	0.026	0.34
502	4.43	0.077	0.42	0.51	0.09	0.012	0.031	0.18
505	8.87	0.084	0.41	0.96	0.16	0.015	0.022	0.55
410	12.34	0.074	0.42	0.19	0.23	0.009	0.005	0.50
308L	19.62	0.020	1.68	0.33	9.88	0.013	0.012	0.52
309L	26.27	0.014	1.43	0.06	12.36	0.020	0.009	0.44

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in Table II. Fluxes C and D were made by adding chromium (III) oxide to two commonly used commercial fluxes while fluxes A and B were made from laboratory grade reagents. All four fluxes were produced by melting in an induction furnace.

Table II. Chemical Composition of Fluxes Used

	Flux A (▼) ⁺	Flux B (■) ⁺	Flux C (▲) ⁺	Flux D (●) ⁺
pct CaO	47.8	39.9	39.8	2.7
pct SiO ₂	41.9	42.9	29.0	42.3
pct MnO	0.1	0.1	0.1	28.9
pct Cr ₂ O ₃	10.2	17.0	18.3	17.8
pct FeO	not detected	not detected	not detected	1.8
pct CaF ₂	—	—	8.7	4.1
pct TiO ₂	—	—	4.1	—
pct S	—	0.045	0.057	0.042
pct P	—	0.045	0.061	0.064
B.I.*	1.00	0.80	1.00	0.35

*B.I. =

$$\frac{\text{MgO} + \text{CaO} + \text{BaO} + \text{SrO} + \text{Na}_2\text{O} + \text{K}_2\text{O} + 1/2(\text{MnO} + \text{FeO})}{\text{SiO}_2 + 1/2(\text{Al}_2\text{O}_3 + \text{Cr}_2\text{O}_3 + \text{TiO}_2 + \text{ZrO}_2)}$$

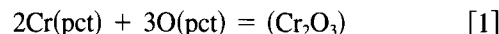
*Flux symbols as used in Figures 1 through 11.

Atomic absorption spectroscopy was used to determine the silicon, manganese, chromium, molybdenum, nickel, and sulfur content of the electrodes as well as the amount of silicon, chromium, manganese, and iron in the fluxes and slags. The weld metal chemical composition was determined by emission spectroscopy, while the oxygen content of the weld metal was determined by vacuum fusion. The sulfur and phosphorous content of the fluxes were determined by wet chemical analysis. Tables III and IV list the chemical analysis for the weld metal and slags, respectively. Also, the spatial distribution of Si, Mn, and Cr in the weld metal was determined with an electron microprobe.

III. EXPERIMENTAL RESULTS AND DISCUSSION

A. Transfer of Chromium

The transfer of chromium may be represented by the equation



The effect of the initial chromium content on the change in chromium content of the weld metal for the different fluxes is shown in Figures 1 and 2. From Figure 1 it can be seen that the neutral point, which is the metal composition at which there is no transfer of chromium between metal and slag, is approximately 8.7 pct for flux D (MnO-Cr₂O₃-SiO₂) and is 19 pct for flux C (CaO-Cr₂O₃-SiO₂) although both the fluxes contained the same amount of Cr₂O₃ initially. It is also interesting to note from Table III that flux A (CaO-SiO₂-Cr₂O₃) containing 10.2 pct Cr₂O₃ produces weld metal with a higher chromium content than flux D (MnO-SiO₂-Cr₂O₃) which contains 17.8 pct Cr₂O₃, clearly indicating the importance of flux type on the transfer of chromium. Figures 2 and 3 indicate that increasing the basicity* of the CaO-Cr₂O₃-SiO₂ type of flux from

*The basicity index (B.I.) of the fluxes is defined as in Table II. However, if other Basicity Indices were used, the general conclusions would still be valid.

0.8 to 1.0 does not appreciably change chromium transfer. Figure 2 also indicates that flux A with 10.2 pct Cr₂O₃ produces weld metal with a chromium content only slightly below that produced when using flux C which is of the

Table III. Chemical Analysis of Weld Metal

Electrode	Flux (B.I.)	Weld No.	Pct C	Pct Mn	Pct P	Pct S	Pct Si	Pct Cr	Pct Ni	Pct Mo	Pct O
505	D (0.35)	1	0.070	0.88	0.022	0.015	0.45	8.73	0.21	0.94	0.090
505	B (0.80)	2	0.11	0.22	0.013	0.017	0.26	11.1	0.12	0.91	0.071
505	C (1.00)	3	0.11	0.21	0.013	0.017	0.25	11.1	0.12	0.90	0.099
505	A (1.00)	4	0.091	0.23	0.015	0.016	0.27	10.5	0.13	0.92	0.065
5151	C (1.00)	5	0.091	0.16	0.012	0.016	0.014	3.29	0.15	0.47	0.090
5151	D (0.35)	6	0.065	0.58	0.026	0.013	0.20	2.97	0.16	0.47	0.048
5151	B (0.80)	7	0.083	0.19	0.014	0.015	0.14	3.25	0.15	0.46	0.071
5212	D (0.35)	8	0.057	0.59	0.033	0.018	0.21	3.38	0.091	0.85	0.047
5212	C (1.00)	9	0.15	0.19	0.019	0.021	0.044	3.62	0.081	0.78	0.106
5212	B (0.80)	10	0.086	0.25	0.019	0.019	0.20	3.57	0.078	0.79	0.090
502	A (1.00)	11	0.14	0.29	0.027	0.018	0.26	6.10	0.21	0.54	0.059
502	C (1.00)	12	0.087	0.18	0.028	0.020	0.24	6.84	0.21	0.54	0.050
502	D (0.35)	13	0.050	0.78	0.038	0.018	0.37	5.18	0.33	0.54	0.050
502*	B (0.80)	14						8.12			0.106
309L	C (1.00)	15	0.050	0.85	0.030	0.010	0.20	23.4	13.7	0.13	0.145
309L	D (0.35)	16	0.050	1.51	0.035	0.010	0.53	21.5	14.1	0.13	0.083
309L	B (0.80)	17	0.082	0.76	0.026	0.011	0.44	23.2	13.0	0.14	0.073
309L*	A (1.00)	18						24.90			0.101
308L	C (1.00)	19	0.045	0.81	0.019	0.010	0.21	20.0	8.83	0.25	0.067
308L	B (0.80)	20	0.064	0.77	0.026	0.012	0.78	19.7	9.36	0.27	0.097
308L	D (0.35)	21	0.045	1.87	0.032	0.010	0.97	17.7	9.86	0.28	0.119
308L	A (1.00)	22	0.093	1.36	0.019	0.012	0.86	19.2	8.64	0.25	0.057
410	B (0.80)	23	0.13	0.22	0.024	0.010	0.40	14.1	0.27	0.21	0.082
410	D (0.35)	24	0.069	0.99	0.043	0.005	0.57	11.8	0.47	0.24	0.057
410	C (1.00)	25	0.10	0.23	0.026	0.010	0.20	13.8	0.28	0.23	0.067

*Wet Chemical Analysis

Table IV. Chemical Analysis of Slags

Weld Number	Pct (SiO ₂)	Pct (Cr ₂ O ₃)	Pct (MnO)	Pct (FeO)	Pct (NiO)
1	42.30	17.80	27.11	4.12	—
2	43.67	11.00	0.72	2.08	—
3	28.43	13.88	0.76	2.46	—
4	40.11	7.15	0.71	1.50	—
5	27.28	13.49	1.03	3.58	—
6	38.44	17.48	24.85	5.18	—
7	42.79	14.12	0.93	2.44	—
8	40.80	14.56	27.04	5.04	—
9	29.81	12.86	0.91	4.39	—
10	46.26	11.71	0.86	2.32	—
11	45.17	6.56	0.67	2.21	—
12	30.34	12.10	0.90	3.80	—
13	45.39	17.87	28.15	3.66	—
14	46.13	12.38	0.98	2.62	—
15	31.88	14.76	2.87	0.63	N.D.
16	39.02	23.09	27.22	2.05	0.12
17	43.59	13.36	2.35	0.62	N.D.
18	44.08	8.20	1.06	0.99	0.14
19	32.53	10.41	2.13	0.53	0.08
20	44.49	12.98	2.40	2.98	0.30
21	42.13	21.51	28.8	2.17	N.D.
22	43.37	7.35	1.57	0.59	N.D.
23	44.59	14.83	0.46	1.44	—
24	40.59	19.73	27.40	4.70	—
25	26.27	16.08	0.48	1.93	—

N.D. = not detected

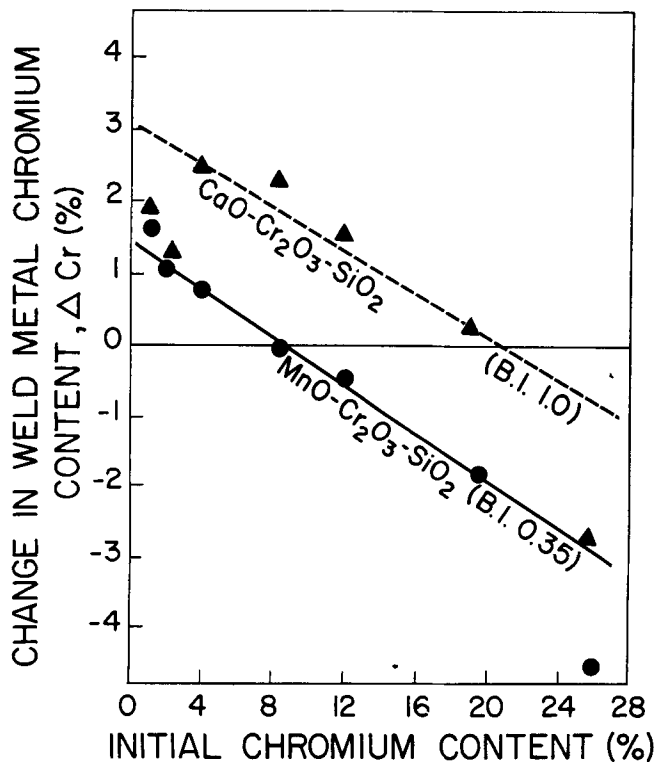


Fig. 1—Change in weld metal chromium content after welding, ΔCr, compared with the initial chromium content of the electrodes for the 2 different flux systems studied.

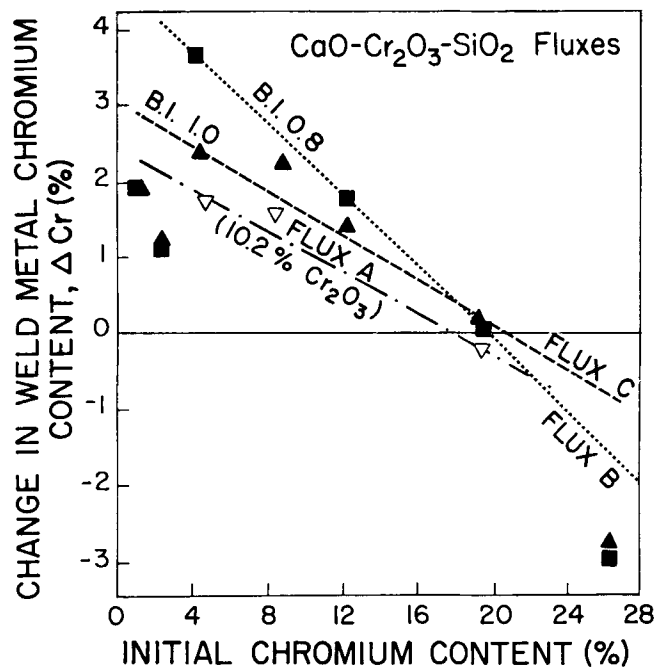


Fig. 2—Change in weld metal chromium content after welding, ΔCr, compared with the initial chromium content of the electrodes for CaO-SiO₂-Cr₂O₃ fluxes.

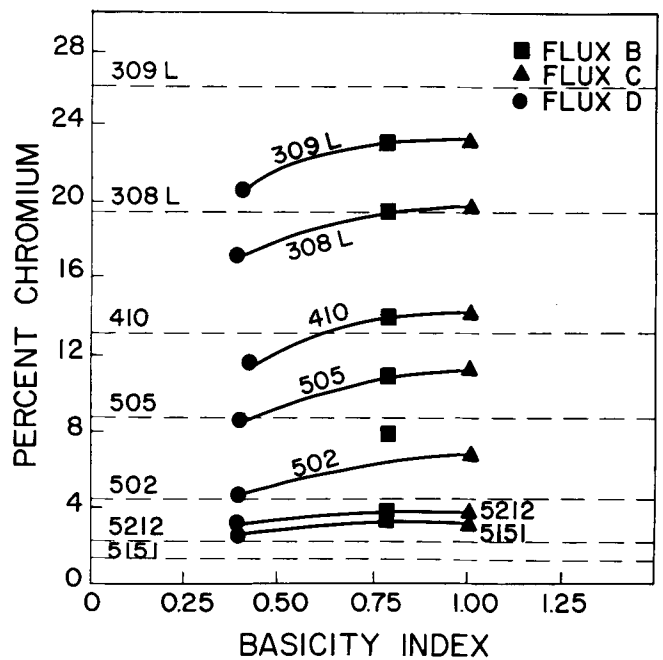


Fig. 3—Variation of the weld metal chromium content with the basicity index of the flux. Dashed lines indicate the initial chromium content of the electrode.

same basicity, but which contains 18.3 pct Cr₂O₃. This is not surprising considering the activity of Cr₂O₃ is near unity in the range 10 pct Cr₂O₃ to 20 pct Cr₂O₃ as seen from the phase diagram for CaSiO₃-Cr₂O₃.¹⁰ Also, a mass balance on chromium, as shown in the Appendix, indicates that due to

the high temperatures involved in welding, there is a loss of chromium by volatilization, especially on using the lime based fluxes. Work by others indicates that chromium (III) oxide volatilizes from silicate mixtures,¹⁰ so the chromium loss is probably from the slag rather than from the weld metal.

B. Transfer of Silicon

The mechanism of transfer of silicon is quite different from the other alloying elements in that there does not seem to be any relationship between the weld metal silicon content and the initial amount of silicon present in the electrodes. This may be observed from Figure 4 which indicates the change in silicon concentration with increasing initial silicon content in the electrodes. A better insight into the mechanism of silicon transfer may be obtained by examining Figures 5 and 6. These figures clearly indicate that the silicon content of the weld metal is not only affected by the basicity of the flux, but also by the chromium content of the electrode. The transfer of silicon may be explained by the reaction:

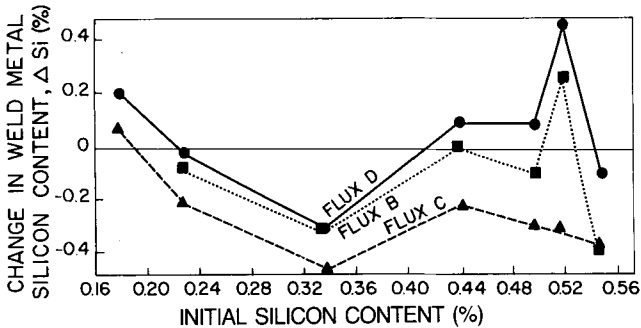


Fig. 4—Change in the weld metal silicon content after welding, ΔSi , compared with the initial silicon content of the electrode, Si .

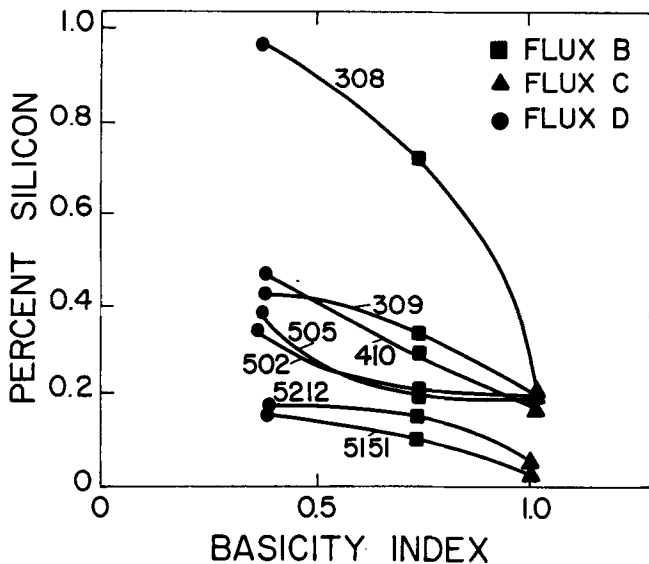


Fig. 5—Variation of the silicon content of the weld metal with the basicity index of the flux.

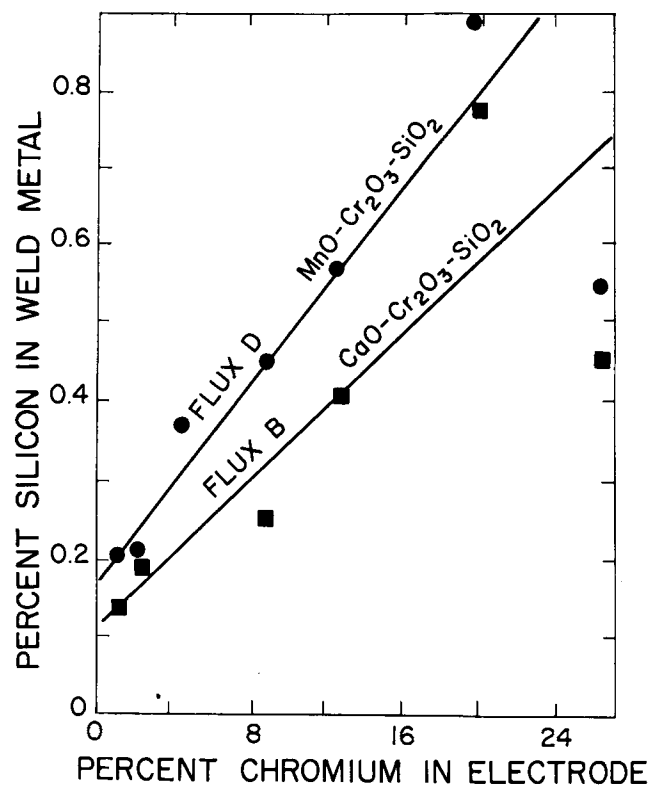
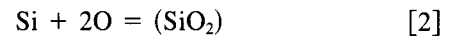
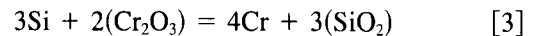


Fig. 6—Variation of the silicon content of the weld metal with initial chromium content of the flux.



As flux basicity is increased, a_{SiO} decreases, thereby reducing the silicon content in the weld metal. Also, as the chromium content of the electrode increases, the activity of oxygen decreases rapidly, thereby increasing the silicon content in the weld metal.

Alternatively, the reaction



may be used to explain the effect of basicity and initial chromium content of the electrode on the silicon content of the weld metal. On increasing flux basicity, a_{SiO} decreases and the reaction proceeds forward, whereas on increasing the chromium content the reaction is reversed. This strong influence of chromium on the weld metal silicon content is responsible for the absence of a singular neutral point in Figure 4.

C. Transfer of Manganese

The transfer of manganese depends mainly on the initial manganese content of the electrode and the flux type. It is not significantly influenced by the other alloying elements present. This is in agreement with work done by other researchers.^{1,2,11} Figure 7 indicates a neutral point of 1.7 pct Mn when using flux D ($MnO-Cr_2O_3-SiO_2$) and approximately zero while using fluxes A, B, and C which contained negligible amounts of MnO. A mass balance presented in

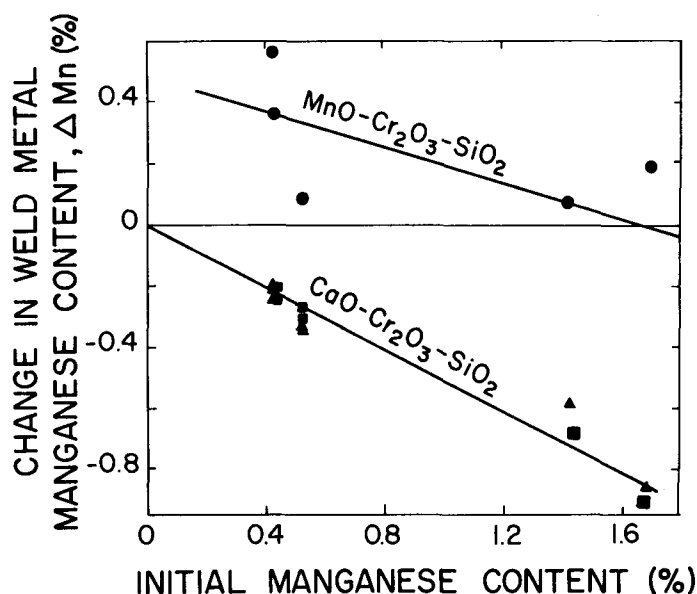


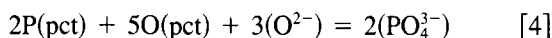
Fig. 7—Change in the weld metal manganese content after welding, ΔM_n , compared with the initial manganese content of the electrode.

the appendix indicates that manganese may be lost by vaporization while welding with electrodes containing high amounts of manganese.

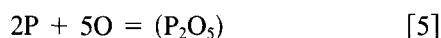
D. Transfer of Phosphorous

As can be seen from Table III, use of fluxes A, B, or C which contain large amounts of CaO resulted in weld metal with a much lower phosphorous content than that produced by flux D which contained MnO.

The transfer of phosphorous may be represented by the reaction¹²



or by



for which the equilibrium constant may be expressed as

$$K = \frac{(X_{\text{P}_2\text{O}_5})(\gamma_{\text{P}_2\text{O}_5})}{(a_{\text{P}})^2(a_{\text{O}})^5} \quad [6]$$

where $X_{\text{P}_2\text{O}_5}$ and $\gamma_{\text{P}_2\text{O}_5}$ are the mole fraction and activity coefficient of phosphorous pentoxide in the slag.

$$a_{\text{P}} = \left[\frac{(X_{\text{P}_2\text{O}_5})(\gamma_{\text{P}_2\text{O}_5})}{(a_{\text{O}})^5(K)} \right] \quad [7]$$

Since substitution of MnO by CaO in the flux could lower $\gamma_{\text{P}_2\text{O}_5}$ by several orders of magnitude,¹² the lower phosphorous content obtained by using lime based fluxes is not surprising. The higher phosphorous content in the weld metal on using flux D could also be due to the higher amounts of phosphorous usually associated with manganese ore, but a semi-quantitative analysis showed that the fluxes contained comparable amounts of phosphorous (see Table II).

E. Transfer of Sulfur

The transfer of sulfur seems to be mainly dependent upon the initial sulfur content of the electrode as shown in Fig-

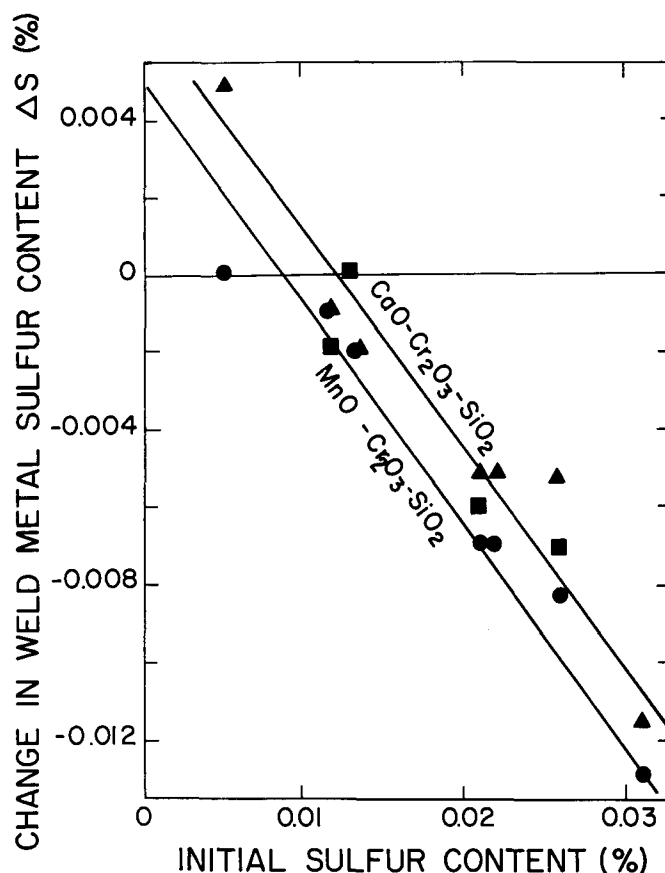
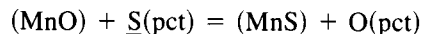


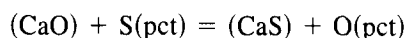
Fig. 8—Change in the weld metal sulfur content after welding, ΔS , compared with the initial sulfur content of the electrode.

ure 8. A neutral point of 0.008 pct S is observed for flux D, and about 0.012 pct S for the other fluxes. The present investigation also showed that use of flux D (B.I. 0.35) produced weld metal with slightly lower sulfur content than that obtained by using the lime silicate fluxes with B.I. (0.8 to 1.0) although some of these fluxes contained the same amount of sulfur initially (see Table II). The results do not agree with the claims of other researchers^{13,14} that the sulfur content of the weld metal depends only on the initial sulfur content of the welding consumables and the basicity index of the flux. This disagreement may be resolved if flux type is taken into account in addition to the above two factors in determining the sulfur content of the weld metal. Flux D was of the MnO-Cr₂O₃-SiO₂ type, and the desulfurization reaction with this flux may be written as



$$G_8 = G_8^{\circ} + RT \ln a_{\text{O}} + RT \ln a_{\text{MnS}} - RT \ln a_{\text{S}} - RT \ln a_{\text{MnO}} \quad [8]$$

For fluxes A, B, and C, which are all lime based, the desulfurization reaction is

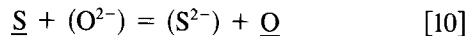


$$G_9 = G_9^{\circ} + RT \ln a_{\text{O}} + RT \ln a_{\text{CaS}} - RT \ln a_{\text{S}} - RT \ln a_{\text{CaO}} \quad [9]$$

In the temperature range 1800 °C to 2000 °C, G_8° is greater than G_9° by approximately +3000 calories, and also the $RT \ln a_{\text{O}}$ term in Eq. [8] may be more positive than the

corresponding term in Eq. [9] due to the higher oxygen potential of flux D; however, these two terms are compensated by the lower value of the term $(-RT \ln a_{\text{MnO}})$ in Eq. [8] as compared to $(-RT \ln a_{\text{CaO}})$ in Eq. [9]. The activity of CaO in fluxes A, B, and C is considerably lower than the activity of MnO in flux D (as can be seen from the activity data in Reference 15), so the term $(-RT \ln a_{\text{MnO}})$ is lower than $(-RT \ln a_{\text{CaO}})$ by about 6000 calories, making G_8 less positive than G_9 .

This approximate thermodynamic calculation indicates that flux D with a B.I. of 0.35 will produce lower sulfur in the weld metal than fluxes A, B, and C and explains the experimental result obtained. Data presented by Davies³ also indicate that manganese silicate fluxes may give better desulfurization than a calcium silicate flux of higher basicity. This confirms the importance of flux type in addition to basicity index in evaluating the desulfurization power of a flux. Also, some welding researchers¹⁶ have claimed that sulfur may be removed by oxidation by the slag. This is unlikely since it has been clearly shown in steelmaking that sulfur is removed by the reduction reaction



and not by oxidation.¹⁷ Thermodynamic considerations indicate that the higher temperatures encountered during welding would make the removal of sulfur by oxidation even less likely than in steelmaking.

F. Transfer of Carbon

It is very difficult to predict the extent of carbon transfer during welding, but usually the weld metal has a lower carbon content than expected from the nominal composition of the electrode and the baseplate, due to oxidation.

Oxidation of the carbon may be represented by the reaction



In the present study, flux D with its higher oxygen potential produced weld metal with a lower carbon content. However, on welding the very low carbon austenitic stainless steel (308L and 309L) with flux D and the CaO-Cr₂O₃-SiO₂ fluxes, the carbon content of the weld metal increased significantly due to carbon pickup from the flux. The carbon in the flux was probably due to induction melting of the flux in a graphite crucible. This may indicate that fluxes containing components which easily form carbides such as Cr₂O₃ or CaO and are prepared in electric arc furnaces may not be suitable for welding austenitic stainless steels, since an increased amount of carbon in these steels promotes intergranular corrosion. The carbon contamination would, of course, be less severe in large commercial furnaces than in small laboratory furnaces.

G. Transfer of Nickel and Molybdenum

During welding of the alloy steels, very little nickel or molybdenum is lost to the slag since these metals are less prone to oxidation than iron. Use of flux D results in a higher amount of nickel in the weld metal; however, it is difficult to draw any conclusions from such sparse data due to possible variations in the nickel content along the length of the wires.¹⁸ The transfer of molybdenum did not depend

on the flux used as the final molybdenum content of the weld metal was almost the same as the molybdenum content of the wire.

H. Oxidation of Iron

The oxidation of iron during submerged arc welding may be represented by the equation

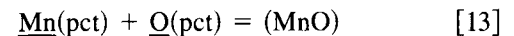


Of the four fluxes used, fluxes A, B, and C were virtually free of iron oxide whereas flux D contained 1.8 pct iron¹¹ oxide initially (Table II). After welding all the slags had increased amounts of iron oxide (Table IV) indicating that Eq. [12] proceeds from left to right. This clearly demonstrates that the oxygen potential of the fluxes used is not controlled by the amount of iron oxide present but by the other oxides, namely, SiO₂, MnO, and Cr₂O₃. The results are consistent with the explanation by Eagar on the sources of oxygen in weld metal.³

I. Effective Reaction Temperature

During welding the metal undergoes a temperature-time cycle, which continuously changes the slag metal equilibrium. However, the changes at lower temperatures may be very small due to slower reaction kinetics, and researchers have often used the term "effective reaction temperature" or "effective equilibrium temperature" at which the experimental mass action index is equal to the equilibrium constant.^{1-3,5,7,11,19}

Considering the Cr (Eq. [1]), Si (Eq. [2]), and Mn reactions,



allows one to compute the thermodynamic equilibrium constants as listed in Table V. Experimental mass action indexes for these three reactions may be defined as

$$K_{\text{exp}} = \frac{(X_{\text{Cr}_2\text{O}_3})}{(\text{pct } \underline{\text{Cr}})^2 (a_{\text{O}})^3} \quad [14]$$

$$K_{\text{exp}} = \frac{(X_{\text{SiO}_2})}{(\text{pct } \underline{\text{Si}}) (a_{\text{O}})^2} \quad [15]$$

$$K_{\text{exp}} = \frac{(X_{\text{MnO}})}{(\text{pct } \underline{\text{Mn}}) (a_{\text{O}})} \quad [16]$$

where $X_{\text{Cr}_2\text{O}_3}$, X_{SiO_2} , and X_{MnO} are the mole fractions, respectively, of Cr₂O₃, SiO₂, and MnO. It is necessary to use the activity of oxygen (a_{O}) rather than (pct $\underline{\text{O}}$) in computing the experimental mass action indexes since for alloy steels the value of (a_{O}) is quite different from (pct $\underline{\text{O}}$) as can be seen from the examples in Table VI. The value of (a_{O}) may be calculated from the chemical composition of the weld metal and the value of the interaction coefficients of the alloying elements present in the steel with oxygen.²⁰ The values of the experimental mass action indexes for reactions [1], [2], and [12] are listed in Table VII. The effective reaction temperature may be estimated by multiplying the mass action indexes by the appropriate values of the activity coefficient of the respective oxides (shown in Table VIII) and comparing these values with those of the

Table V. Values of the Thermodynamic Equilibrium Constants for the Chromium, Silicon, Manganese, and Iron Reactions (from References 15, 19)

Equilibrium Constant K	Equation Relating K and T	Values of K at Different Temperatures			
		$T = 1873$ K (1600 °C)	$T = 2073$ K (1800 °C)	$T = 2273$ K (2000 °C)	$T = 2473$ K (2200 °C)
$K = \frac{a_{Cr_2O_3(s)}}{[a_{Cr}]^2[a_O]^3}$	$K = \exp\left(\frac{98918}{T} - 43.2\right)$	14951	91.20	1.38	0.04
$K = \frac{a_{SiO_2(l)}}{[a_{Si}][a_O]^2}$	$K = \exp\left(\frac{65301}{T} - 24.43\right)$	34009	1177	89.92	7.21
$K = \frac{a_{MnO(l)}}{[a_{Mn}][a_O]}$	$K = \exp\left(\frac{28480}{T} - 12.3\right)$	18.08	4.17	1.20	0.45

Table VI. Example of the Difference in Activity of Oxygen and the Weight Percent Oxygen for Welds Made with Different Electrodes

Electrodes	Weld Number	(Pct O)	$[a_O]$
5151	5	0.090	0.066
505	3	0.099	0.035
410	23	0.082	0.019
309L	18	0.101	0.009

Table VIII. Value of Activity Coefficients of Various Oxides in the Slags at 1000 °C

Oxide	Flux A	Flux B	Flux C	Flux D
Cr ₂ O ₃	12 to 15	7 to 9	5 to 8	—
SiO ₂	0.4 to 0.5	0.4 to 0.5	0.4 to 0.5	0.4 to 0.5
MnO	0.6 to 0.8	0.6 to 0.8	0.6 to 0.8	0.33 to 0.40

Table VII. Range of Values of the Experimental Mass Action Indices for the Chromium, Silicon, and Manganese Reactions Obtained by Using the Different Electrodes for the Four Fluxes Studied

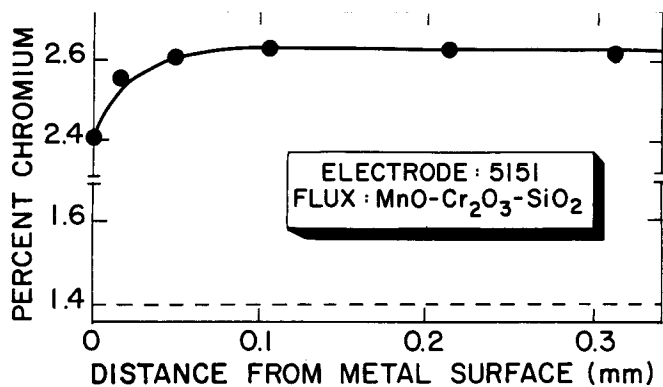
Experimental Mass Action Index	Flux A	Flux B	Flux C	Flux D
$K_{exp} = \frac{X_{Cr_2O_3}}{[pct Cr]^2[a_O]^3}$	45 to 580	15 to 323	22 to 260	167 to 680
$K_{exp} = \frac{X_{SiO_2}}{[pct Si][a_O]^2}$	1503 to 10291	8645 to 16283	928 to 15550	1277 to 4069
$K_{exp} = \frac{X_{MnO}}{[pct Mn][a_O]}$	0.88 to 1.64	0.64 to 3.92	0.64 to 2.62	9.62 to 18.4

equilibrium constants listed in Table V. This procedure leads to an effective reaction temperature in the range 1700 to 2000 °C. The activity data for SiO₂ and MnO for the flux systems CaO-Cr₂O₃-SiO₂ and MnO-Cr₂O₃-SiO₂ are not available, but since the interaction between SiO₂ and CaO, and SiO₂ and MnO would be far greater than that with Cr₂O₃, activity data for the CaO-SiO₂ and MnO-SiO₂ systems were utilized.¹⁵ Since the activity of Cr₂O₃ is near unity for the CaO-Cr₂O₃-SiO₂ systems,¹⁰ there is some justification for the above assumption. Data for the activity of Cr₂O₃ in the MnO-Cr₂O₃-SiO₂ system are not available. Also, the thermodynamic data utilized for determining the activity coefficients of the oxides and for computing the activity of oxygen are valid only for a temperature of 1600 °C (activity data at higher temperatures are not available). Calculations by Belton¹⁹ for the activity of SiO₂ in the system CaO-SiO₂ indicate that the value of the activity coefficient of SiO₂ may decrease by 30 to 50 pct on increasing the temperature from 1600 °C to 2000 °C. However, this change in the value of the activity coefficient is small when compared with the large variations in the experimental mass action indexes (see Table VII). These variations in the experimental mass

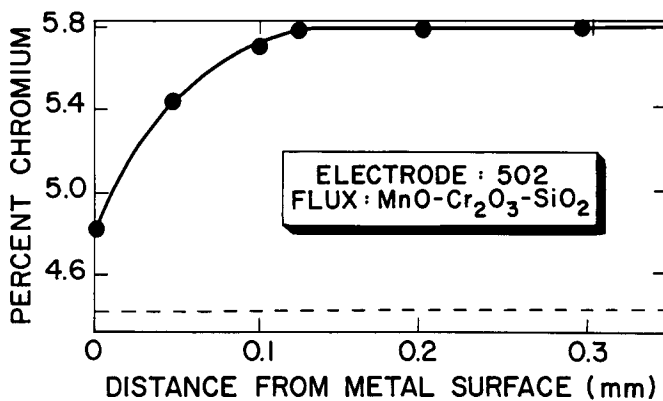
action indexes are mainly responsible for the wide range of effective reaction temperatures (1700 to 2000 °C), and it may indicate that the bulk slag and metal do not always reach equilibrium. Results of ongoing research seem to support this view.³⁰

J. Spatial Distributing of Chromium, Silicon, and Manganese in the Weld Metal

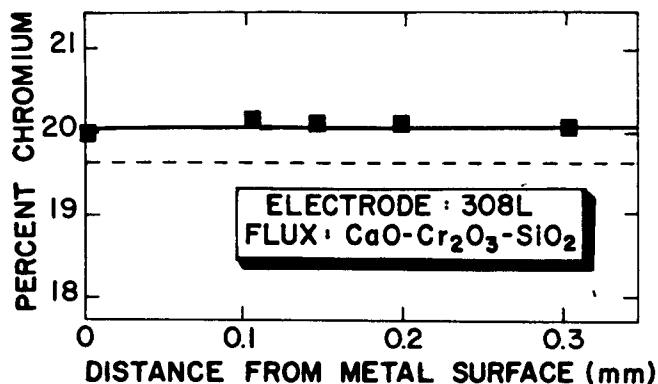
The distribution of Cr, Si, and Mn in several weld metals is shown in Figures 9, 10, and 11. Generally, there is a zone of alloy depletion near the slag-metal interface, although for the austenitic stainless steels the chromium content of the steel increases near the slag metal interface. Since alloying elements are being transferred from the slag to the metal in most of the welds the depletion zones of the alloying elements cannot be explained by the bulk transfer of the alloying elements. The depletion zones are most likely due to surface reactions occurring at lower temperatures between the cooling molten weld pool and the slag. Further evidence of these surface reactions is suggested by the presence of a strongly adherent slag film on the weld metal



(a)



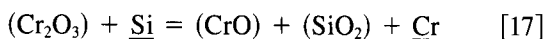
(b)



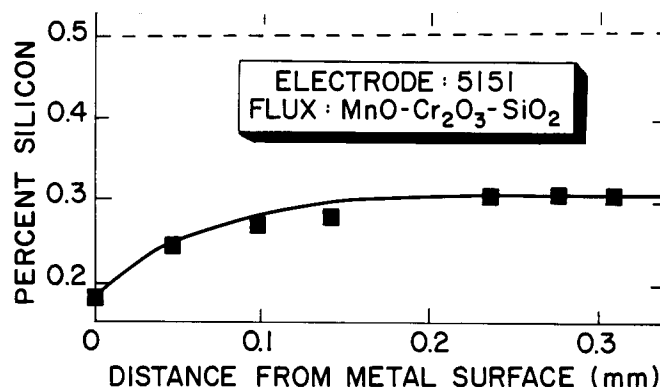
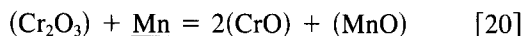
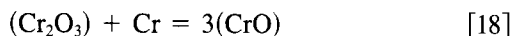
(c)

Fig. 9—(a) Spatial distribution of chromium in weld metal no. 6. Dashed line indicates the initial composition of the electrode. (b) Spatial distribution of chromium in weld metal no. 13. Dashed line indicates the initial composition of the electrode. (c) Spatial distribution of chromium in weld metal no. 20. Dashed line indicates the initial composition of the electrode.

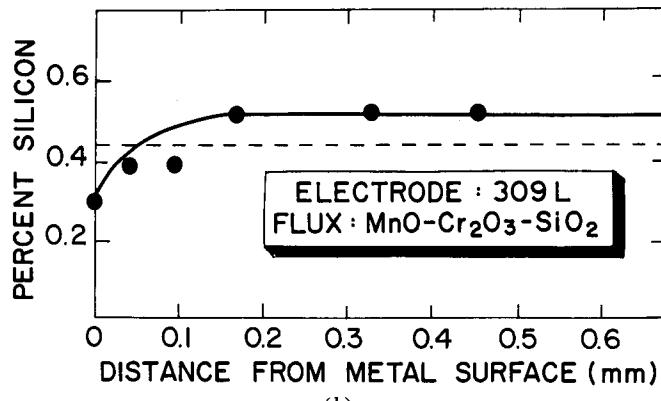
surface which is rich in chromium. An electron microprobe analysis of the adherent slag film on weld no. 21 is indicated in Table IX. It is likely that reactions such as



which are quite rapid even at 1500 to 1600 °C,²¹ take place. Other reactions such as



(a)



(b)

Fig. 10—(a) Spatial distribution of silicon in weld metal no. 6. Dashed line indicates the initial composition of the electrode. (b) Spatial distribution of silicon in weld metal no. 16. Dashed line indicates the initial composition of the electrode.

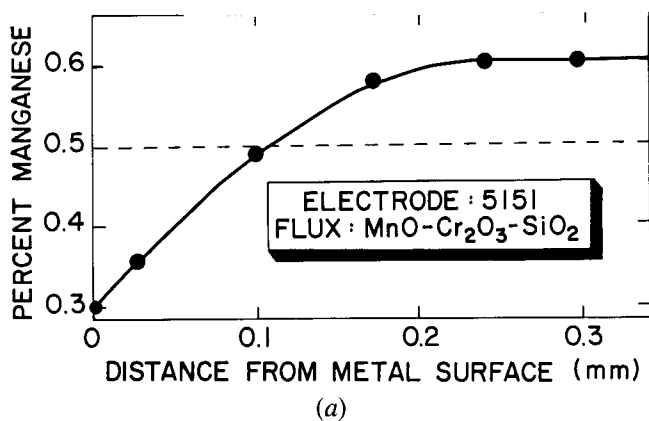
may also be important. This is in agreement with work done by other researchers.^{22,23,24} The depletion of manganese and silicon may also be due to the greatly increased stability of MnO and SiO₂ at lower temperatures.¹¹

The observed drop in the concentration of manganese, silicon, and chromium at the weld metal surface may be due either to reactions between the cooling molten weld pool and the slag or to reactions between the solid metal and the slag. The former case would be valid if the effective reaction temperature (but not the temperature of the cooling weld pool) were in the range of 1800 to 2000 °C so that the surface concentration of the alloying elements would drop

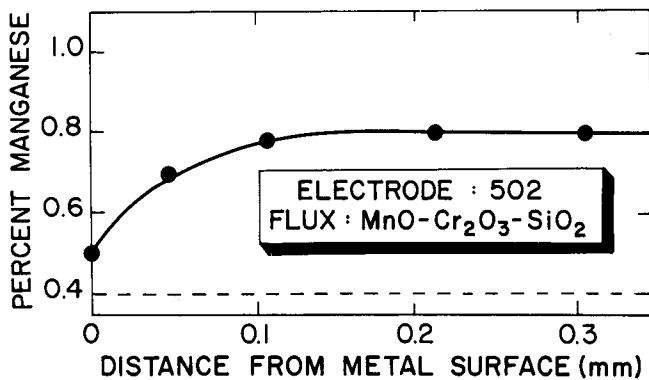
Table IX. Results of the Microprobe Analysis of the Film of Slag Formed on the Surface of Weld No. 21

Element	Oxidation State of Element in the Mineral Used as Standard	Phase 1	Phase 2
		Wt Pct Oxide	Wt Pct Oxide
Si	4	37.11	10.74
Ca	2	3.78	0.64
Cr	3	23.03	77.14*
Mn	2	31.37	16.59
Fe	2	0.54	7.45
TOTAL		96.83	112.56*

*Indicates that the oxidation state of Cr in the sample may be lower than 3 leading to a total greater than 100 pct.²⁹



(a)



(b)

Fig. 11—(a) Spatial distribution of manganese in weld metal no. 6. Dashed line indicates the initial composition of the electrode. (b) Spatial distribution of manganese in weld metal no. 13. Dashed line indicates the initial composition of the electrode.

significantly when the temperature reached 1500 °C. If, however, the effective reaction temperature is around 1600 °C as suggested by some researchers,³ then the drop in the concentration of alloying elements at the surface may only be explained by reactions occurring at a much lower temperature. If the concentration of the alloying elements at the surface and in the bulk are assumed constant, then a solution to Fick's second law of diffusion allows one to estimate the width of the depleted layer at which the concentration is the mean of the surface and bulk concentrations. This is given as

$$X_{\bar{c}} = \sqrt{Dt} \quad [21]$$

where $X_{\bar{c}}$ is the mean of the surface and bulk concentrations. If diffusion is taking place in the liquid metal, then the solidification time for the experimental conditions used is on the order of two seconds.²⁵ If diffusion was occurring in solid metal, then $t = 10^2$ seconds. Using tabulated values of the diffusion coefficient,^{26,27,28} $X_{\bar{c}}$ may be calculated for both solid and liquid metal. Table X lists these values along with the experimentally observed values of this investigation and of the work done by Christensen.¹¹ It can clearly be observed from Table X that the values of $X_{\bar{c}}$ for liquid metal are much closer to the experimental values, and the calculated $X_{\bar{c}}$ for solid metal is two to three orders of magnitude lower than that observed from the experimental data. This analysis clearly indicates that the reactions during the cooling period occur between molten metal and slag.

IV. CONCLUSIONS

The effect of slag-metal reactions on the transfer of various elements present in low alloy and stainless steels has been investigated and has resulted in the following conclusions:

1. The transfer of chromium is strongly dependent on the type of flux used. Lime silicate fluxes produced weld metal with a much higher chromium content than manganese silicate fluxes, although both fluxes contained the same amount of chromium (III) oxide.
2. The transfer of silicon is greatly influenced by the basicity index of the flux used as well as by the initial chromium content of the electrode. The lower the basicity index of the flux and the greater the initial chromium content of the electrode, the greater will be the amount of silicon in the weld metal.
3. The manganese content of the weld metal depends mainly on the amount of manganese oxide in the flux and the initial manganese content of the electrode. The amount of the other alloying elements present does not appear to have significant influence on the transfer of manganese.
4. The desulfurizing capability of a flux should be judged by the flux type, the basicity index, and the initial amount of sulfur present in the flux. The MnO-Cr₂O₃-SiO₂ flux (B.I. 0.35) gave slightly better desulfurization than the CaO-Cr₂O₃-SiO₂ type fluxes (B.I. 0.8 to 1.0).

Table X. Calculated Values of the Diffusion Distance $X_{\bar{c}}$ at Which the Concentration of the Alloying Element in the Weld Metal Is Midway between Surface and Bulk Concentrations, as Compared with the Experimentally Observed Values of $X_{\bar{c}}$

Alloying Element	Calculated Values of $X_{\bar{c}}$ (in cms)				Experimental Values of $X_{\bar{c}}$ (in cms)	
	Liquid Metal (at 1500 °C)		Solid Metal (at 1250 °C)		Present Investigation	Christensen's Work ¹¹
	D_L in cm ² /s	$X_{\bar{c}} = 0.9538\sqrt{2D_L}$	D_s in cm ² /s	$X_{\bar{c}} = 0.9538\sqrt{100D_s}$		
Manganese	4.9×10^{-5}	9.5×10^{-3}	1.25×10^{-10}	1.11×10^{-5}	8×10^{-3} 15×10^{-3}	10×10^{-3} 50×10^{-3}
Silicon	2.4×10^{-5}	6.6×10^{-3}	$\approx 10^{-10}$	$\approx 10^{-5}$	8×10^{-3} 12×10^{-3}	—
Chromium	0.9×10^{-5}	4.2×10^{-3}	3.8×10^{-10}	1.95×10^{-5}	5×10^{-3} 15×10^{-3}	—

5. The lime based fluxes produced weld metal with a lower phosphorous content than that produced by using the flux containing manganese oxide. This may be due to the stronger dephosphorizing power of lime.
6. The carbon content of the weld metal depended strongly on the type of flux used. Use of the MnO-Cr₂O₃-SiO₂ flux resulted in a lower carbon content in the weld metal due to the higher oxidizing potential of these fluxes. The low carbon austenitic steels picked up carbon from the fluxes.
7. The effective reaction temperatures for reactions between chromium, silicon, and manganese, with dissolved oxygen, lies in the range 1700 to 2000 °C.
8. Almost all the nickel and molybdenum is transferred from the electrode to the weld metal.
9. When the weld pool cools, surface reactions take place between the slag and the metal. These reactions result in a drop in the concentration of the alloying elements at the weld metal surface due to the reduction of chromium (III) oxide to lower oxides.
10. Surface reactions take place between the slag and the cooling molten metal and not between the slag and solid metal. The existence of this reaction zone of cooling molten metal and slag confirms the earlier conclusions that the effective reaction temperature is over 1700 °C.
11. Welds made with electrodes containing high amounts of manganese may lose manganese by vaporization. During welding, chromium loss also occurs, but this is most likely due to volatilization of chromium oxide from the slag.

APPENDIX

Mass balance of chromium and manganese

The chromium loss by vaporization from both the slag and the metal is given by the following equation:

$$\text{Chromium loss} \approx \frac{M(Cr_i - Cr_f)}{100} + \frac{S[(Cr_2O_3)_i - (Cr_2O_3)_f]}{100} \times \frac{2(A.W.)_{Cr}}{(M.W.)_{Cr_2O_3}}$$

- where
- M = wt of weld metal (in g)
 - S = wt of slag (in g)
 - Cr_i = initial chromium concentration in metal (pct)
 - Cr_f = final chromium concentration in metal (pct)
 - $(Cr_2O_3)_i$ = initial concentration of Cr₂O₃ in flux (pct)
 - $(Cr_2O_3)_f$ = final concentration of Cr₂O₃ in flux (pct)
 - $(A.W.)_{Cr}$ = atomic weight of chromium = 52
 - $(M.W.)_{Cr_2O_3}$ = molecular weight of Cr₂O₃ = 152

Substitution of the appropriate values for the terms in the right-hand side yields positive values from 0.07 g for weld no. 2 to 1.38 g for weld no. 17. It was also noted that the

chromium loss is maximum with austenitic stainless steel welds made with lime silicate fluxes. For these welds both of the terms on the right-hand side of the above expression were positive. Work by others¹⁰ suggests that chromium may be volatilizing as an oxide from the slag.

By using an expression similar to the one above, the amount of manganese loss was also computed. The loss in manganese was more pronounced for electrodes containing a high amount of manganese initially, and the loss occurred when both calcium silicate and manganese silicate fluxes were used. Values ranged from 0.0 grams for weld no. 2 (electrode 505) to 0.19 g for weld no. 16 (electrode 309L) when using calcium silicate fluxes. For manganese silicate fluxes values ranged from 0.0 g (electrode 505) to 0.12 g for weld no. 15 (electrode 309L). It will be noted that electrode 309L has high Mn while electrode 505 has the lowest Mn and hence the lowest Mn vapor pressure.³¹

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