Effect of Electrochemical Reactions on Submerged Arc Weld Metal Compositions

Weld metal composition is controlled by chemical reactions in four separate areas during welding

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ABSTRACT. The purpose of this work is to investigate the relative influence of electrochemical and thermochemical reactions on the weld metal chemistry in a direct current submerged arc welding process. Chemical analyses were carried out on the detached droplets and the weld metal for both electrode-positive (reverse) polarity where the welding wire is anodic and electrode-negative (straight) polarity where the welding wire is cathodic. The results suggest that both thermochemical and electrochemical reactions are important in altering the composition of the weld metal. The anodic electrochemical reactions include the oxidation of iron and alloy elements, and the discharge and pickup of oxygen anions from the molten flux. Cathodic electrochemical reactions include the reduction of iron and alloy elements from the flux to the metal phase, and the refining of oxygen. Thermochemical reactions occur and move the overall composition toward the thermochemical equilibrium.

Introduction

The submerged arc welding process uses a protective flux cover with a consumable welding wire. The welding current is carried largely by the submerged arc and to some extent by conduction in the molten flux layer. Information on the interaction between slag and weld metal is significant for a better understanding of the arc welding process. Although slag/weld metal reactions are of importance in many fusion welding processes and are often referred to in the literature, comparatively little is known about the mechanisms that control them.

The chemistry in steel making tends to be dominated by thermochemical reactions because they generally involve large surface areas, low current densities and alternating current power. But a direct current submerged arc welding process involves small surface areas and high current densities. Therefore, it is expected that electrochemical reactions, as well as thermochemical reactions, will exert a significant influence over the final chemistry of the weld.

The overall composition of the weld is controlled by the composition of the metal droplets that enter the weld pool and by the amount of dilution of the weld pool by the base plate. These compositions are controlled by chemical reactions at four separate zones: the melted electrode tip, the detached droplet, the hot weld pool immediately below the arc, and the cooling and solidifying weld pool behind the arc. Thermochemical reactions occur at all four zones and move the chemistry in the direction of chemical equilibrium. But electrochemical reactions occur only at the melted electrode tip and in the hot weld pool immediately below the arc. The electrochemical reactions would result from ionic conduction of a portion of the welding current through the molten slag layer. Therefore, only thermochemical reactions are expected to occur at the surface of the detached droplets and solidifying weld pool since these parts are no longer carrying current.

The most important chemical considerations for submerged arc welding include the control of oxygen, oxidation losses of alloy elements, and the pickup of undesirable elements from the slag. A number of investigations have been made concerning the interaction between the slag and the metal in submerged arc welding of steel. Most of these investigations were based solely on thermochemical reactions (Refs. 1-9), although lately a few investigators have considered the electrochemical reactions that occur when direct current is used in welding. Frost (Ref. 10) considered the different chemical effects at the anode and cathode in electroslag welding. Blander and Olson (Ref. 11) postulated an electrochemical mechanism for the alteration of weld metal chemistry in submerged arc welding.

Electrochemical and Thermochemical Reactions

Electrochemical reactions could be an important factor governing the chemistry of weld metal in direct current welding. Electrochemical effects can occur at the interfaces of the slag with the hot weld pool and the melted electrode tip. The relative numbers of ions and electrons in the slag govern the importance of these effects, which could be major factors controlling weld metal chemistry. When liquid slag has an interface with the molten metal, the electrochemical reactions are relatively simple to understand. This type of interface is present in submerged arc welding. The possible anodic reactions include the oxidation of iron and alloy elements, and the discharge and pickup of oxygen anions from the slag

\[ M \text{(metal)} + n\text{O}^{2-} \text{(slag)} = MO_n \text{(slag)} + 2n\text{e}^- \]

where \( M \) is iron or an alloy element at the electrode tip/slag or the weld pool/slag interface. Thus, substantial oxidation losses of alloy elements and pickup of oxygen are expected at the anode. The
Due to the high temperature, it is thermodynamically possible for chemical reactions to occur. A number of investigations have been made concerning the nature of chemical reactions at the melted electrode tips and the detached droplets (Refs. 5, 8, 12-18), and several investigators indicated that oxygen was transferred to the metal in these two zones (Refs. 2, 3, 13, 14, 18). In the hot weld pool immediately below the arc, the detached droplets become "diluted" with molten metal from the base plate. Although the slag/metal interfacial contact area available for reaction is much smaller than that of the detached droplets, the strong turbulence existing in the hot weld pool creates an effective stirring of the liquid metal. Moreover, pickup of oxygen at this zone is favored by the increased time available for reaction. It is believed that the pickup of oxygen is the result of the oxygen solubility being exceeded in the hot weld pool. The zone of the molten weld pool behind the electrode starts to cool and solidify as the electrode moves away from it. Upon cooling of the metal in the weld pool from a high temperature to the solidification temperature, a supersaturation with respect to silicon and manganese deoxidation reactions occurs initially. Therefore, silicon and manganese will react with dissolved oxygen, and then the composition will move rapidly towards equilibrium.

In addition to the electrochemical reactions, thermochemical reactions also play an important role in controlling the weld metal chemistry in submerged arc welding. The thermochemical reactions occur very rapidly because of high temperature. These thermochemical reactions include deoxidation reactions, such as those encountered in steel making, and reactions that lead to a closer approach to equilibrium between the flux and metal phase. Examples of such reactions would be silicon pickup from a high silica flux or the oxidation loss of transition elements.

$$\text{SiO}_2 \text{(slag)} + 2\text{M(metal)} = \text{Si(metal)} + 2\text{M} \text{(slag)}$$  \hspace{1cm} (5)

$$\text{FeO} \text{(slag)} + \text{M(metal)} = \text{Fe(metal)} + \text{MO} \text{(slag)}$$  \hspace{1cm} (6)

where M can be aluminum or calcium in Reactions 5 and 6 and manganese in Reaction 6 for the flux system used in this research. The droplet forms at the electrode tip and then travels through the molten flux and plasma. The entire process occurs in a few milliseconds (Refs. 12, 13), and the temperature of the droplet is very high. Due to the high temperature, it is thermodynamically possible for chemical reactions to occur. A number of investigations have been made concerning the nature of chemical reactions at the melted electrode tips and the detached droplets (Refs. 5, 8, 12-18), and several investigators indicated that oxygen was transferred to the metal in these two zones (Refs. 2, 3, 13, 14, 18). In the hot weld pool immediately below the arc, the detached droplets become "diluted" with molten metal from the base plate. Although the slag/metal interfacial contact area available for reaction is much smaller than that of the detached droplets, the strong turbulence existing in the hot weld pool creates an effective stirring of the liquid metal. Moreover, pickup of oxygen at this zone is favored by the increased time available for reaction. It is believed that the pickup of oxygen is the result of the oxygen solubility being exceeded in the hot weld pool. The zone of the molten weld pool behind the electrode starts to cool and solidify as the electrode moves away from it. Upon cooling of the metal in the weld pool from a high temperature to the solidification temperature, a supersaturation with respect to silicon and manganese deoxidation reactions occurs initially. Therefore, silicon and manganese will react with dissolved oxygen, and then the composition will move rapidly towards equilibrium.

Figure 1 shows the schematic of expected variations in oxygen and silicon contents for an electrode-positive (reverse polarity) submerged arc weld due to thermochemical and thermochemical reactions. The curve shows the oxygen and silicon contents of steel in equilibrium with solid silica at some temperature. Before experiments were done, the composition variation was expected to follow the straight lines for an electrode-positive submerged arc weld. The anodic reaction at the melted electrode tip causes some oxygen pickup and silicon loss. The thermochemical reactions cause more oxygen pickup at the melted electrode tip and the detached droplet while the droplet is passed through the molten flux. At the cathodic weld pool, oxygen refining and silica reduction were expected, and then weld composition would vary with travel speed due to the difference in the amount of thermochemical deoxidation reaction. As the welding speed decreases, the amount of thermochemical deoxidation reaction increases because the heat input and the solidification time increase. Therefore, weld pool composition was expected to go to equilibrium composition as the travel speed decreases.

**Experimental Procedure**

Direct current electrode-negative (straight) and direct current electrode-positive (reverse polarity) submerged arc welds were made with 2.38 mm (1/32 in.) commercial low-carbon steel welding wire on ASTM A36 steel plates and a water-cooled pure copper plate. The compositions of the steel plate and the welding wire are given in Table 1, and the composition of the commercial flux used is shown in Table 2.

Figure 2 is a schematic drawing of a cross-section of the submerged arc welding process showing the melted electrode tips, the detached droplets and the base plate for both electrode-positive and electrode-negative polarities. The melted electrode tips, detached droplets and weld metal were collected and analyzed. The water-cooled copper plate was used as a base plate to collect the melted electrode tips and the detached droplets. The welding process was operated at a constant welding current of 385 A and a constant potential of 28.5 V. The constant current...
was obtained by adjusting the electrode velocity, which was 72 mm/s (170 in./min) for the anodic wire, and 99 mm/s (235 in./min) for the cathodic wire.

The electrode tips were collected by stopping the welding process, pulling the electrode away from the weld pool and cutting off the tip. The liquid metal droplets were released from the electrode tip and travel through the molten flux. The detached droplets were collected from welds made at a high velocity over a water-cooled copper plate so that the droplets are suspended in the molten flux. The detached droplets were extracted from the ground slag by magnetic separation. The speed of quenching attained is sufficient to freeze the metal composition established at high temperature. Single pass, bead-on-plate welds were made on steel plates at several welding speeds (1.55–3.467 mm/s) with constant voltage (28.5 V) and current (580 A) for both polarities. The wire feed speed was adjusted to maintain the constant current.

Analyses for oxygen were carried out using a LECO interstitial analyzer, i.e., fusion in a graphite crucible under inert atmosphere. A Baird — Atomic emission spectrometer was used to determine manganese, silicon and other alloy elements in weld metals, welding wire and electrode tips. The electrode tips and wires were flattened in a rolling mill to get enough area for analysis. The detached droplets were analyzed using the wavelength dispersive analyzer on a JEOL scanning electron microscope.

A metallurgical model by Their (Ref. 5) is adopted to show the extent of element transfer between the weld metal and flux. Its application gives quantitative data for the gain or loss of elements arising from slag/metal reactions. The transfer efficiency into the weld can be expressed in terms of the difference between analytical and nominal compositions. The difference between analytical and nominal compositions is defined as delta (Δ) quantity. The analytical composition is obtained by chemical analysis methods and the nominal composition can be obtained by calculations based on the detached droplet and plate compositions and dilution. A positive concentration change (Δ > 0) indicates a gain or pickup of a particular element, i.e., transfer of element from the slag to the weld metal. A negative change (Δ < 0) indicates a loss, i.e., transfer from the weld metal to the slag.

### Results and Discussion

The purpose of this investigation is to consider the relative influence of thermochemical and electrochemical reactions on the weld metal chemistry. Electrochemical reactions are expected because of the high current densities, and thermochemical reactions are expected because of the high temperature and the generally large temperature-dependent differences in chemical potentials of the various reactants and products in the flux and metal phases.

An examination of the welding wire, steel plate and flux compositions in Tables 1 and 2 shows that the wire and steel plate have very low silicon and oxygen concentrations, and a relatively high manganese concentration, while the flux has a high silica activity and a relatively low manganese-oxide/iron-oxide ratio, which is far from equilibrium with the welding wire and steel plate. Thus, the manganese content of the welding wire and steel plate would be expected to drop as a result of thermochemical oxidation losses to the flux, and the silicon and oxygen content would be expected to increase because of the reaction with the flux.

The reactions at the melted electrode tip, the detached droplet and the weld pool were considered. The chemical analysis results show that a substantial difference exists between the chemistries of wire and flux. These differences are the result of electrochemical reactions.

Figure 3 shows the plot of the average oxygen contents of the welding wire, the melted electrode tips, and the detached droplets for both electrode-negative and electrode-positive polarity welding modes. This plot shows a very low oxygen content in the welding wire (20 ppm) and a very significant oxygen pickup in the melted electrode tips for both polarities. The influence of thermochemical oxygen pickup is shown by the fact that significant oxygen pickup is observed in both electrode-positive and electrode-negative configurations. This excess oxygen came from the surrounding atmosphere and decomposition of oxide components in the flux. The influence of electrochemical reactions is shown by the fact that the oxygen content of the anode in the electrode-positive polarity power mode (591 ppm) is over twice that of the cathode in the electrode-negative polarity power mode (277 ppm). This oxygen content difference is due to oxygen pickup at the anode and oxygen refining at the cathode. The real difference is somewhat less since more wire is fed and melted at the cathode for a fixed current, thus diluting the total electrochemical and thermochemical effect at the cathode. If the electrochemical and thermochemical reactions were considered as separate steps, the average melted electrode tip oxygen concentration for the two polarities could be considered to crudely represent the thermochemical contribution, and the separation of two concentrations from this mean would represent the electrochemical effects. However, the different wire feed rates cloud this interpretation. After the
molten droplet separates from the wire, the electrochemical reaction ceases. But the thermochemical reaction continues while the droplet is falling through the molten slag. Therefore, the detached droplet shows higher oxygen content than the melted electrode tip due to the increase in oxygen content by the continuous decomposition of flux. Even though electrochemical reaction does not occur in detached droplets, the results of oxygen analysis still show the electrochemical reaction effect at the melted electrode tips as indicated by the difference in oxygen contents between anodic and cathodic droplets.

Figures 4 and 5 show the average silicon and manganese contents in the initial electrode, the melted electrode tip and the detached droplet. The melted electrode tips show the increases in silicon concentration (less increase at the anode and more increase at the cathode) and the decreases in manganese concentration (less decrease at the cathode and more decrease at the anode) for both polarities. This is evidence that both thermochemical and electrochemical reactions occurred at the melted electrode tip. The initial welding wire has a very low silicon content, while the flux has a high silicon-oxide content. This causes the thermochemical pickup of silicon from the flux. The electrochemical influence is significant, as indicated by the fact that the cathodic electrode tip silicon content is about 0.06 wt% higher than that of the anodic electrode tip, and by the fact that the cathode feed rate is higher than the anode feed rate, which means the total amount of silicon in the cathodic electrode tip is relatively higher than indicated in Fig. 4. Both thermochemical and electrochemical reactions are also indicated in the case of manganese; however, the high manganese content in the electrode and the low manganese-oxide (MnO)/iron-oxide (Fe2O3) ratio in the flux lead to thermochemical manganese loss at the melted electrode tip. Therefore, manganese oxidation and silicon reduction reactions are major thermochemical reactions in this system. The changes in the silicon and manganese concentrations from the electrode tip to the detached droplet are mostly thermochemical. With silicon, however, there is a decrease rather than an expected increase in silicon content of the detached droplet compared to the melted electrode tip, indicating that a large fraction of the silicon in the droplet has back reacted with more noble metal oxides in the flux (e.g., Fe2O3). One of the possible driving forces for this reaction is related to the possibility that the droplet is at a lower temperature and has a higher oxygen content than the tip. The average manganese content is further decreased by thermochemical reactions with more noble metal oxides in the flux when going from the electrode tip to the detached droplet, which falls through and reacts with the flux.

Figure 6 compares the detached droplet compositions for the various alloy elements. Silicon, aluminum and manganese are the major elements that react with the flux. The flux contains a high silicon-oxide content, which causes the thermochemical pickup of silicon from the flux. The aluminum and manganese contents in the droplet decrease due to their reaction with the flux. The electrochemical reaction is significant, as indicated by the fact that the cathodic electrode tip aluminum content is about 0.06 wt% higher than that of the anodic electrode tip, and by the fact that the cathode feed rate is higher than the anode feed rate, which means the total amount of aluminum in the cathodic electrode tip is relatively higher than indicated in Fig. 4. Both thermochemical and electrochemical reactions are also indicated in the case of manganese; however, the high manganese content in the electrode and the low manganese-oxide (MnO)/iron-oxide (Fe2O3) ratio in the flux lead to thermochemical manganese loss at the melted electrode tip.
show higher concentrations in the cathodic droplets than in the anodic droplets. This is largely caused by oxidation losses to the flux at the anode and electrochemical reduction from the flux at the cathode during the reaction at the melted electrode tip. The differences for nickel, titanium and chromium are of the order of the analytical uncertainties and are thus inconclusive. Molybdenum shows the opposite trend. That is, the concentration in the anode is higher than that of the cathode. This behavior is difficult to explain in terms of molybdenum reaction alone, but if iron reaction is also taken into account, it can be explained easily. Iron is the major electrode constituent and it is more easily oxidized than molybdenum. Therefore, the loss of iron at the anode and the gain of iron at the cathode are relatively greater than those of molybdenum, and these cause an increase in molybdenum concentration at the anode and a decrease at the cathode. Thus, this behavior of molybdenum is also the result of electrochemical reaction.

Figures 7 through 14 show the results of chemical analyses of the anode and cathode weld metal for silicon, manganese, aluminum, molybdenum and oxygen as a function of welding speed. The results for the anode and cathode of each element are plotted together. These results show that electrochemical reactions cause substantial changes in weld metal chemistry.

Figure 7 illustrates the variations in delta silicon due to polarity. High transient concentration of oxygen may exist in the liquid metal at the hot weld pool as a result of high solubility at elevated temperature.

On slow cooling down to the solidification temperature, this will lead to spontaneous reaction and losses of dissolved silicon. The silicon loss must be due to the formation of some deoxidation reaction product. It is generally accepted that formation of silicon oxide (SiO₂) takes place when sufficient oxygen is available. But silicon loss is recovered by electrochemical reduction reaction at the cathode and increased at the anode by electrochemical oxidation reaction. Therefore, silicon shows much loss at the anode, and a little gain or almost no change at the cathode.

Figure 8 shows the variations in delta manganese due to polarity. Similar to silicon, oxidation of manganese is favored by the lower temperature prevailing in the cooler part of the weld pool. Here, manganese will react with dissolved oxygen to form slags that exhibit a large loss of manganese in both anode and cathode weld metal. The reason why manganese shows extensive losses in both cases is because the flux has a little manganese oxide (MnO) and the base plate has a high manganese content. Therefore, manganese can be oxidized easily. Another reason for manganese loss can be a result of the evaporation because vapor pressure increases strongly with temperature. But the difference in delta manganese due to polarity shows the effect of electrochemical reaction. That is, the cathode shows less loss than the anode because of the electrochemical reduction reaction at the cathode, and the electrochemical oxidation reaction at the anode.

Variations in delta aluminum are shown in Fig. 9. Aluminum, like silicon and manganese, is also oxidized while the temperature of the weld pool is lowered to the
solidification temperature. Aluminum oxide (Al₂O₃) is stable at high temperature rather than silicon oxide (SiO₂) and manganese oxide (MnO), as indicated in the Ellingham diagram. Therefore, even though the flux contains a large amount of aluminum oxide, it is difficult to pick up the aluminum from the slag by electrochemical reduction reaction at the cathode weld pool. So, the results show the aluminum losses even at the cathode weld pool. But the lesser loss at the cathode is the evidence for the electrochemical reaction.

Figure 10 shows the variations in delta molybdenum due to polarity. Molybdenum changes show the opposite trend as in the melted electrode tip. This behavior of molybdenum is the result of iron losses at the anode and pickup at the cathode as discussed previously. Figures 11 through 13 show the variations in delta nickel, chromium, and titanium due to polarity. Those elements also show a little electrochemical effect. But the differences between anode and cathode are of the order of the analytical uncertainties and are thus inconclusive.

Figure 14 shows the variations in delta oxygen due to polarity. Oxygen losses are shown at both cathode and anode, and the cathode shows less loss than the anode. This is the result of the difference in the slag/metal interfacial contact area available for deoxidation reaction. The area of the cathode is smaller than that of the anode. Therefore, the separation of deoxidation products at the anode is easier than that at the cathode. Thus, electrochemical effect may be swept out by thermochemical reaction.

Figure 15 is the composition map for both electrode-negative and electrode-positive polarity submerged arc welding, showing the variations in oxygen and silicon contents during welding. The curves are the plots of the silicon and oxygen contents of steel in equilibrium with solid
silica at 1600°C (2912°F) and 1800°C (3272°F). The compositions of welding wire, melted electrode tips, detached droplets and weld metal are plotted on the diagram for both polarities. The wire has low silicon and oxygen contents. Both anodic and cathodic electrode tips show an increase in silicon content due to the oxidation of iron and manganese, and in oxygen content due to decomposition of flux and contamination from the atmosphere. But the cathodic electrode tip shows a greater increase in silicon and less increase in oxygen, due to the electrochemical silicon reduction and oxygen refining reactions. While the detached droplets are falling through the molten flux, the droplets pick up the oxygen by flux decomposition and contamination from the atmosphere. Therefore, the oxygen contents in the droplets are higher than those in the electrode tips for both polarities. The weld metal shows decreases in silicon and oxygen contents by deoxidation reaction and composition variation due to welding speed. As the welding speed decreases, the composition of the weld metal approaches the equilibrium composition.

Conclusions
1) Both electrochemical and thermochemical reactions are significant in submerged arc welding.
2) The thermochemical reactions move the flux and weld metal compositions toward chemical equilibrium. In this study, manganese activity was higher in the metal than in the flux; therefore, manganese oxidation loss from the metal to the flux was observed. Silicon activity was higher in the flux; therefore, a thermochemical silicon pickup by the weld metal was observed.
3) The electrochemical reactions at the anode include oxidation losses of alloy elements to the flux and the discharge and pickup of oxygen anions from the flux. The electrochemical reactions at the cathode include the reduction of metal ions from the flux and the refining of oxygen.
4) Thermochemical and electrochemical composition changes are greater at a low than at a high welding speed. Electrochemical reactions are enhanced by higher, total current flow per unit volume of weld metal. Thermochemical reactions at a low welding speed are enhanced by higher temperatures and longer reaction time before solidification.
5) Composition paths for the silicon-oxygen equilibrium are different for direct current electrode-positive (reverse polarity) and direct current electrode-negative (straight polarity) welds.
6) The total gain or loss of alloy elements in weld metal is influenced by the compositions of flux, electrode and base plate, and by welding process conditions. Further experiments with synthetic fluxes, which are chosen to minimize thermochemical reactions, are planned and should help to better define the relative importance of electrochemical reactions.

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References


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In October 1987, the PVRC Steering and Technical Committees on Piping Systems established a task group on independent support motion (ISM) to evaluate the technical merits of using the ISM method of spectral analysis in the design and analysis of nuclear power plant piping systems.

The results of the task group evaluation culminated in a unanimous technical position that the ISM method of spectral seismic analysis provides more accurate and generally less conservative response predictions than the commonly accepted envelope response spectra (ERS) method, and are reported in this WRC Bulletin. The price of WRC Bulletin 352 is $25.00 per copy, plus $5.00 for U.S., or $10.00 for overseas, postage and handling. Orders should be sent with payment to the Welding Research Council, 345 E. 47th St., Room 1301, New York, NY 10017.

WRC Bulletin 354
June 1990

The two papers contained in this bulletin provide definitive information concerning the elevated temperature rupture behavior of 21/4Cr-1Mo weld metals.

(1) Failure Analysis of a Service-Exposed Hot Reheat Steam Line in a Utility Steam Plant
By C. D. Lundin, K. K. Khan, D. Yang, S. Hilton and W. Zielke

(2) The Influence of Flux Composition of the Elevated Temperature Properties of Cr-Mo Submerged Arc Weldments
By J. F. Henry, F. V. Ellis and C. D. Lundin

The first paper gives a detailed metallurgical failure analysis of cracking in a longitudinally welded hot reheat pipe with 184,000 hours of operation at 1050°F. The second paper defines the role of the welding flux in submerged arc welding of 2 1/4Cr-1Mo steel.

Publication of this report was sponsored by the Steering and Technical Committees on Piping Systems of the Pressure Vessel Research Council of the Welding Research Council. The price of WRC Bulletin 354 is $50.00 per copy, plus $5.00 for U.S. and $10.00 for overseas postage and handling. Orders should be sent with payment to the Welding Research Council, 345 E. 47th St., Room 1301, New York, NY 10017.