ELECTROCHEMICAL REACTIONS AT THE ELECTRODE IN SUBMERGED ARC WELDING

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ABSTRACT

The submerged arc welding process uses a D.C. arc under a protective slag cover to melt a consumable wire electrode. The purpose of this work is to investigate the relative influence of electrochemical and thermochemical reactions at the surface of the electrode of the composition on the liquid metal droplet. Chemical analyses were carried out on the melted wire electrode tips and on the detached droplets for both reverse polarity (wire is anodic) and straight polarity (wire is cathodic) polarities. The results suggest that both thermochemical and electrochemical reactions are important in altering the composition of the detached droplet.

INTRODUCTION

The submerged arc welding process consists of a consumable electrode, an electrically conducting slag and a work piece. Figure 1 shows a schematic drawing of the submerged arc welding process, which is complex and characterized by large currents, large gradients of temperature, and four complex phases. The flux is fed to the plate surface ahead of the weld, and the arc and weld pool are protected from the atmosphere by a molten flux layer. The welding current is carried largely by the submerged arc and to some extent by conduction in the molten flux layer. The overall composition of the weld is controlled by the composition of the metal droplets which enter the weld pool, by the amount of dilution of the weld pool by the parent plate, and by electrochemical and thermochemical reactions at the weld pool/slag and electrode/slag interfaces before solidification takes place. Three chemical reaction sites and two generic reaction mechanisms are available.
for modification of the weld metal composition by reaction with the slag. Both thermochemical and electrochemical reactions are expected to occur at the electrode tip. The electrochemical reactions would result from ionic conduction of a portion of the welding current through the molten slag layer. Only thermochemical reactions are expected to occur at the surface of the detached droplets since the droplets are no longer carrying current. The molten metal in the weld pool is influenced by both electrochemical and thermochemical reactions with the slag before solidification occurs.

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. The objective of this work was to understand the nature and extent of electrochemical and thermochemical reactions at the electrode tip and in the detached droplets.

A number of investigations have been made concerning the nature of chemical reactions at the electrode tip and in the detached droplets. These include work by Pokhodnya and Kostenko (1), Potapov and Lyubauskii (2), Norin and Malyshev (3), Grong and Christensen (4), Mitra (5), and Lau et al. (6). However, few investigators have considered the electrochemical reactions that occur when direct current is used in welding. Frost et al. (7) considered the different chemical effects at the anode and cathode in electroslag welding. Blander and Olson (8) postulated an electrochemical mechanism for the alteration of weld metal chemistry in submerged arc welding. The purpose of this research is to investigate the importance of electrochemical reactions in controlling the chemistry of weld metal 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 flux

$$\text{M(metal)} + n\text{O}^{2-} \text{(slag)} \rightarrow \text{MOn} + 2\text{ne} \tag{1}$$

where M is iron or an alloy element at the electrode tip/slag interface. The possible cathodic reactions include the reduction of metal ions from the flux, and, to some extent, the refining of nonmetallic elements such as oxygen and sulfur

$$\text{M}^{2+} \text{(slag)} + 2\text{e}^- = \text{M(metal)} \tag{2}$$

$$\text{Si}^{+4} \text{(slag)} + 4\text{e}^- = \text{Si(metal)} \tag{3}$$

$$\text{O(metal)} + 2\text{e}^- = \text{O}^{2-} \text{(slag)} \tag{4}$$

where M and Si represent electrodeposited metals at the interface.

The thermochemical reactions at the electrode tip are rapid because of the high temperatures in the vicinity of 1800 to 2000°F. These include deoxidation
reactions, such as those encountered in steel making, and reactions which 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 through a deoxidation reaction

\[
\text{SiO}_2\text{(slag)} + 2\text{M(metal)} = \text{Si(metal)} + 2\text{MO(slag)} \quad (5)
\]

\[
\text{FeO(slag)} + \text{M(metal)} = \text{Fe(metal)} + \text{MO(slag)} \quad (6)
\]

where M can be Al or Ca in reactions (5) and (6) and Mn in reaction (6) for the flux system used in this research. Once the molten droplet separates from the electrode, the electrochemical reactions stop, and compositional changes occur only by thermochemical reactions. The objectives of this research are to evaluate the nature and relative extent of the electrochemical and thermochemical reactions which occur at the electrode and in the molten droplets in the submerged arc welding process.

**EXPERIMENTAL PROCEDURE**

Straight (cathodic electrode wire) and reverse (anodic electrode wire) polarity submerged arc "welds" were made with a commercial low-carbon steel welding wire (2.38 mm) on a pure copper plate. The compositions of the welding wire and the commercial flux are given in Table I.

The welding process was operated in both straight and reverse polarity at a constant welding current of 585 amperes and a constant potential of 28.5 volts. The constant current was obtained by adjustment of the wire electrode velocity which was 170 inches/minute for the anodic wire and 235 inches/minute for the cathodic wire. The electrode tips were collected by stopping the welding process and pulling the electrode away from the weld pool. The separated droplets were collected by magnetic separation after running the weld at a high velocity over a water cooled copper plate so that the droplets remained suspended in the molten flux.

Chemical analyses of the alloy elements in the electrode tips were carried out by rolling the tips to produce flat specimens and analyzing with an emission spectrograph. The compositions used for comparison are averages of the compositions for several electrode tips. The separated droplets were analyzed using the wave length dispersive analyzer on a JEOL scanning electron microscope. The reported analyses are an average of the compositions for several droplets. Analyses for oxygen were carried out using a LECO interstitial analyzer.
RESULTS AND DISCUSSION

The purpose of this investigation was to consider the relative influence of thermochemical and electrochemical reactions on the composition of the liquid metal droplet. Electrochemical reactions are expected because of the high current densities, and thermochemical reactions are expected because of the high temperatures and the generally large and temperature dependent differences in chemical potentials of the various reactants and products in the flux and metal phases. An examination of the metal and flux compositions in Table I. shows that the electrode has very low silicon and oxygen concentrations, and a relatively high manganese concentration, while the flux has a high silica activity and a relatively very low manganese oxide/iron oxide ratio, which is far from equilibrium with the wire. Thus, the manganese content of the metal would be expected to drop through thermochemical oxidation losses to the flux, and the silicon and oxygen content in the metal would be expected to increase through reaction with the flux.

Figure 2 shows a plot of the average oxygen contents of the wire, the electrode tip, and the separated droplets for both straight (cathodic wire electrode) and reverse (anodic wire electrode) polarity welds. The data show a very low oxygen content in the electrode (20 ppm) and very significant oxygen pickup in the electrode tip from both thermochemical and electrochemical reactions. The influence of electrochemical reactions is shown by the fact that the oxygen content of the anode tip in the reverse polarity power mode (591 ppm) is over twice that of the cathode in the straight polarity power mode (277 ppm). 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. 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. Since the electrode tip is, on the average, halfway to becoming a droplet, the droplets should start with, very roughly, twice the oxygen content of the tip.

If the electrochemical and thermochemical reactions were considered as separate steps, the average electrode tip oxygen concentration for the two polarities could be considered to crudely represent the thermochemical contribution, and the separation of the two concentrations from this mean would represent the electrochemical effects. However, the different wire feed rates cloud this interpretation. The average oxygen concentration for the two electrode tips is 434. This can only crudely represent the substantial thermochemical pickup above the 20 ppm oxygen present in the initial electrode.

Figure 3 shows the silicon contents in the initial electrode, the electrode tip, and the separated droplet. The analyses suggest significant contributions from both thermochemical and electrochemical reactions. The wire electrode has a
very low oxygen content of around 0.002 wt %, while the flux has a SiO₂ content of about 11.22 wt %. This causes the thermochemical pickup of around 0.19 wt % silicon from the flux. The electrochemical influence is significant, as is indicated by the fact that the cathodic tip silicon content is about 0.06 wt % higher than that of the anodic tip and by the fact that the cathode feed rate is higher than the anode feed rate which means that the total amount of Si in the cathodic tips and droplets is relatively much higher than is indicated in Figure 3.. The change in the silicon concentration from the electrode tip to the detached droplet is mostly thermochemical. With silicon, however, there is a decrease rather than the expected increase in silicon content of the droplet compared to the 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 probability that the droplet is at a lower temperature and has a higher oxygen content than the tip.

Figure 4 shows similar behavior for the manganese contents in the electrode, the electrode tip, and the detached droplet. Both thermochemical and electrochemical reactions are indicated; however, the high manganese content in the electrode and low MnO/iron oxide ratio in the flux lead to a thermochemical manganese loss at the electrode tip. The average manganese content is further decreased by thermochemical reactions with more noble metal oxides in the flux in going from the electrode tip to the separated droplet, which falls through and reacts with the flux.

Figure 5 compares the droplet compositions for the various alloy elements to the initial electrode contents. Significant electrochemical reactions are present for most of the alloy elements. Silicon, aluminum, and manganese 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. 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 may be caused by the fact that molybdenum is more noble than iron, and the apparent concentration changes are the result of iron oxidation losses at the anode and reduction from the flux at the cathode. Figure 5 suggests significant thermochemical contributions only in the cases of silicon, aluminum, and manganese.

1. Composition changes at the electrode tip and in the separated droplets in submerged arc welding appear to be the result of both thermochemical and electrochemical reactions.
2. The thermochemical reactions are caused by expected reactions between the flux and metal. 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.

3. Composition changes in the droplets after separation from the submerged arc electrode are primarily thermochemical in nature.

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.

ACKNOWLEDGMENTS

Three authors (J.H.K., R.H.F., and D.L.O.) wish to acknowledge the support of the U.S. Army Research Office at the Colorado School of Mines and M.B. acknowledges the support of the Office of Naval Research at Argonne National Laboratory under Navy Order No. N00014-85-F-0097.

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Table I. Compositions of Weld Wire and Welding Flux (wt %)

| Weld Wire  | Welding Flux  |
|------------|---------------|
|            | SiO₂          |
| C          | 0.06          |
| Mn         | 1.38          |
| Si         | 0.05          |
| SiO₂       | 11.22         |
| Mo         | 0.33          |
| Al₂O₃      | 18.14         |
| Cr         | 0.07          |
| MgO        | 33.23         |
| Ni         | 0.11          |
| CaF₂       | 25.26         |
| Cu         | 0.77          |
| MnO        | 1.15          |
| Al         | 0.02          |
| TiO₂       | 0.90          |
| Cr         | 0.02          |
| Fe₂O₃      | 1.99          |
| P          | 0.012         |
| S          | 0.015         |
| O          | 0.002         |
| N          | 0.004         |
| S          | 0.003         |
| O          | 0.001         |
| N          | 0.004         |
Fig. 1. Schematic of the submerged arc flux welding process.

Fig. 2. Average oxygen contents of the initial weld wires, the electrode tips, and the separated droplets for both straight (cathodic wire) and reverse (anodic wire) polarities.
Fig. 3. Average silicon contents in the initial weld wires, electrode tips, and the separated droplets for both straight and reverse polarities.

Fig. 4. Average manganese contents in the initial weld wires, electrode tips, and the separated droplets for both straight and reverse polarities.
Fig. 5. Average droplet compositions for Si, Al, Ni, Cr, Mo, Ti, and Mn for straight and reverse polarities compared with the initial weld wire compositions.