Toward Developing a SMA Welding Electrode for HSLA-100 Grade Steel

Keeping heat input constant, flux components were varied to find the best combination of performance and mechanical properties

BY D. A. FLEMING, A. Q. BRACARENSE, S. LIU, AND D. L. OLSON

ABSTRACT. A sequential flux coating formulation methodology was used to study the effects of welding flux type on high-strength steel weld metal microstructure and properties. Systematic variations in flux composition were made starting with an initial flux that can be classified as rutile-based and ending up with a more basic flux. The objective of these variations was to identify/develop a formulation of a SMA welding electrode flux that would exhibit the excellent welding behavior found typically in a rutile electrode, balanced with the superior weld metal properties deposited by a basic electrode.

Nine separate series of electrodes were investigated, each with one substitution for a specific component in the flux. The electrode that produced the best results for a given series was used as the basis for the formulation of the next series. The best experimental electrode formulated produced welds exhibiting an estimated yield strength of approximately 800 MPa (120 ksi) and acceptable toughness at -60°C (-76°F) in single-pass welds. The weld metal fracture appearance at this temperature was predominantly ductile. The microstructure of this weld deposit was characterized by 60 vol-% acicular ferrite and 30 vol-% lath martensite. The dual-phase microstructure and the 2:1 acicular ferrite-to-martensite volume ratio were results of controlled additions of titanium in the weld metal, at approximately 150 ppm. The weld metal oxygen was approximately 400 ppm.

The synergistic effects of weld metal oxygen and weld metal alloy content were characterized to develop an understanding of the deoxidation reactions that occurred in the weld pool. The oxygen-alloying content relationship observed in this program can be used as a basis to modify weld metal composition and design consumables to produce weld metals meeting specific weld metal property requirements.

KEY WORDS
SMA Welding
HSLA Steel Welding
Weld Pool Deoxidation
Electrode Formulation
Pec Equation
Dual Phase Microstruct.
Acicular Ferrite
Martensite
Weld Metal Impact Tough.
Weld Fracture

Introduction
The welding of high-strength low-alloy (HSLA) steel has gained significant importance during the past twenty years as structural requirements demand steels with higher strength to reduce section size and weight. A combination of eutectoidal decomposition and property enhancement due to microalloying addition has provided HSLA-100 steel with excellent strength and toughness properties. The welding of HSLA-100 steel is the primary concern in this research. In particular, this study addresses the formulation of a base composition of a shielded metal arc (SMA) welding electrode for joining HSLA-100 steel plates. The challenge of welding HSLA steels lies in controlling the weld metal microstructure, as well as developing a consumable that performs adequately in all positions. Also important is the reduction and/or elimination of pre- and postweld heat treatment to reduce production costs. The metallurgical development of the weld metal microstructure and properties is the major focus of this research.

Weld Metal Microstructure
HSLA steels are typically characterized with very low carbon content to improve their weldability. The mechanical properties of HSLA-100 steel are basically achieved by solid solution strength-
ening, precipitation strengthening and microstructural transformation to bainite and martensite. Because of the intricate relationship between microstructure and thermal experience, one of the major problems in welding HSLA-100 steel is its microstructural instability during the thermal cycle of welding.

To achieve successful shielded metal arc welds of HSLA-100 steel with properties comparable to those of the original plate, a consumable with excellent properties is required. The electrode must produce weld metal with proper microstructure to give both sufficient strength and toughness.

Acicular ferrite is the weld metal constituent that has been reported to best promote toughness in HSLA steels with around 500 MPa (72 ksi) yield strength because of the random orientation of the ferrite laths and their ability to deflect cracks during propagation (Refs. 1–6). As such, a large amount of acicular ferrite optimizes the weld metal mechanical properties. Factors considered in the nucleation and growth of acicular ferrite are as follows (Ref. 7):

1) Chemical composition of the weld deposit.
2) Chemical composition of inclusions (mainly oxides).
3) Size distribution of inclusions.
4) Crystallographic and thermal disregistry between inclusions and the matrix.

Intragranular transformation of austenite to acicular ferrite is favored when large prior austenite grains exist, which occurs when the inclusion density is low or when the inclusion sizes are greater than the Zener diameter, and grain boundary pinning sites are limited; and nonmetallic, intragranular inclusions are available for acicular ferrite nucleation. In addition to inclusion size, size distribution and chemical composition of second phase particles are important. However, an excessively low oxygen content, and thus a small inclusion population, will likely result in insufficient nuclei for acicular ferrite formation, and possibly leading to a haminic microstructure.

To understand weld metal phase transformations, it is essential to know the weld metal oxygen content. Oxygen has a very low solubility in iron, suggesting that the oxygen found in the weld metal occurs as inclusions, which will have a variety of sizes and compositions (Ref. 8). A majority of these inclusions form as a result of different deoxidation steps in the liquid weld pool, with the final inclusions forming interdendritically during solidification (Refs. 9–11). It is these inclusions that affect the formation of weld metal ferrite.

In the case of an HSLA-100 steel, gas tungsten arc welding at 1.3 kJ/mm produced weld metals of high hardness (35 HRc) and of microstructure consisting of martensite and bainite (Ref. 12). The mechanical properties of this type of weld metal microstructure can be improved by introducing acicular ferrite laths to create small packets of martensite and bainite. The behavior of these martensite/bainite packets resembles that of refined grains, which enhances strength and improves toughness. Similar behavior was observed in HY-130 steel weldments by Ramsay, et al. (Ref. 13). Based on these observations, the development of acicular ferrite in HSLA-100 steel weldments is of great importance and must be promoted.

Factors That Control Weld Metal Oxygen

The molten flux that is transferred to the weld pool will act as a slag cover for the weld bead. However, some of the oxides formed as a result of weld pool deoxidation may be trapped in the weld metal during solidification in the form of inclusions (e.g., silicates, aluminates, titanium) and affect subsequent solid-state transformations (Ref. 9). Since these deoxidation reactions will occur rapidly due to the high temperatures and large interfacial areas available for reaction (Refs. 14, 15), an understanding of the mechanisms that control weld metal oxygen is essential to the formulation of electrodes.

One important concept related to the various chemical reactions that occur during welding with electrodes covered by flux is the basicity of the slag or "basicity index" (Refs. 16–18). The basicity index is an empirical index developed to describe the metallurgical behavior of a slag, even though imperfectly. It has also been correlated with the amount of oxygen present in a weld metal. Higher basicity fluxes generally result in welds of lower oxygen content. And it is based on these experimental evidences that basicity index has also been related to the ability of oxides in a welding flux to dissociate into a metallic cation and a metallic oxiad. Oxides which dissociate easily are termed basic, while those which dissociate only to a small degree are termed acidic. The more common oxides in slags can be arranged according to their relative acidity or basicity as follows:

Increasing basicity ⇒

\[
\begin{align*}
B_2O_3, SiO_2, P_2O_5, Al_2O_3, TiO_2, ZrO_2, FeO, MgO, MnO, CaO, Na_2O, K_2O
\end{align*}
\]

However, the definition of basicity of an oxide is not absolute. In fact, any oxide in the series shown above will react as a base with any oxide that is more acidic in nature (to its left) and vice-versa.

As a result of still incomplete understanding of the thermodynamic properties of the slags, the empirical concept of basicity has been developed to predict flux and weld properties. Basicity index (BI) is determined by the ratio between basic and acidic ingredients, and may be estimated using the following equation (Refs. 18–22):

\[
E = \frac{CI}{2}
\]

In the above equation, each basic or acidic ingredient is represented by its mass percent in the flux. According to the International Institute of Welding interpretation, a flux is acidic when the basicity index is less than 1; neutral when it is between 1.0 and 1.5; semibasic when it is from 1.5 to 2.5; and basic when the index is greater than 2.5 (Ref. 20). It was found that in general the higher the basicity, the cleaner the weld metal with respect to nonmetallic inclusions, that is, lower weld metal oxygen content. Although a nonoxide, CaF_2 has been included in the basicity index equation as a basic ingredient because of its ability of dissociation in Ca^{4+} and F^− ions. (For additional discussion on basicity index, see Refs. 15, 18, 19, 46.)

Alloying elements in the weld metal will have a significant effect on the final microstructural phases present by affecting the hardenability and by reacting with oxygen to form inclusions, which serve as nucleation sites within the weld metal. These elements can also strengthen the weld metal through solid solution or precipitation strengthening (Ref. 1). The weld metal composition is directly affected by alloy additions from the flux or specially alloyed core rods used. Dilution of the base plate will also add alloying elements to the weldment. Each of the alloying elements will have an effect on the final weld metal properties. The individual effect is sometimes difficult to determine due to the synergistic effects of other additions.

Manganese, the primary weld metal alloy addition, stabilizes austenite to lower temperatures, which may lead to the formation of bainite and martensite. It is also suggested that manganese forms inclusions, for example, μ-phase (MnOAlO_2), which acts as nucleation sites for acicular ferrite (Refs. 23, 24). The presence of acicular ferrite balances with the formation of harder phases to result in a microstructure that is characterized by both high strength and high tough-
ness. Since manganese may promote toughness through the formation of inclusions, and subsequently nucleation of acicular ferrite, the weld metal oxygen content will strongly influence the effectiveness of manganese as a "strengthening/toughening" agent. Therefore, the level of manganese within a given flux system must be adjusted to achieve optimal properties.

Titanium and boron have been reported to improve the mechanical properties for weld metals (Refs. 25-30). The nucleation of grain boundary ferrite can be suppressed with the proper balance of boron and titanium. Many mechanisms have been proposed to explain the action of boron in controlling the nucleation of grain boundary ferrite (Refs. 31-36). Among them, one mechanism suggests that boron, as a free element, will diffuse to the prior austenite grain boundary and reduce grain boundary energy. This lowering of energy leads to an increase in the energy barrier to nucleation of ferrite and reduction of grain boundary ferrite. Titanium protects boron from nitrogen and oxygen. Titanium nitride forms at a higher temperature than boron nitride and will allow boron to remain free to diffuse to the prior austenite grain boundaries. Titanium-containing inclusions have also been found to be advantageous for the nucleation of intragranular acicular ferrite.

Over the years, attempts have been made to provide calculated quantities to characterize the weldability of steels, either in general terms, or to cover specific types of cracking or other important aspects of welding behavior. Most of these expressions are empirical and attempt to weigh the effect of each alloy element in order to provide a means of comparing alloying systems. The researchers who have published on this aspect are Dearden and O'Neill over fifty years ago (Ref. 37). More recently, their formula was simplified by the International Institute of Welding (IIW) to give the IIW formula for "carbon equivalent" (CE or \( CE_{\text{IIW}} \)):

\[
CE_{\text{IIW}} = C + \frac{Si}{30} + \frac{Mn + Cu + Cr}{20} + \frac{Ni}{60} + \frac{Mo + V}{15} - \frac{5B}{10}
\]

(3)

Compared with the IIW formula, the \( P_{\text{cm}} \) formula gives an increased importance to carbon and recognizes the contribution of boron. It should be noted that oxygen is absent from this equation, even though it is known to have a marked effect on the weld metal properties. Attempts have been made by Jones, et al. (Ref. 41), and Onsoien, et al. (Ref. 42), to incorporate the effect of oxygen in empirical predictive equations such as the ones introduced earlier.

A general criticism of using these weldability expressions is that they consider only the chemical composition of the material and not the cooling rate. \( P_{\text{cm}} \) and CE\(_{\text{IIW}} \) can only be effectively used for correlation of alloy content to hardenability if constant heat input is being used. More recent efforts in HAZ studies have developed weldability expressions that include cooling rate. Yurioka, et al. (Ref. 43), Duren and Lorentz (Ref. 44), and Klukken, et al. (Ref. 45), are some of the researchers who have published on this aspect.

Weld Pool Pyrometallurgy

The final weld metal chemical composition is determined by the slag-metal reactions that occur in the weld pool (Refs. 9, 46-49). Research into slag-metal reactions has generally been done within the limited scope of a single flux system. However, the complexity of the welding environment, as well as the nonideal behavior of the reactions that occur in the arc, lead to too many variables, which makes accurate modeling of the effect of specific changes in system parameters difficult. Even small changes in the flux coating can result in large variations in the behavior of the flux system, which in turn leads to large variations in the metallurgical processes occurring in the weld pool.

Due to the variance of the welding environment with changing welding conditions, such as the type of power sources and flux systems used, the resulting weld pool chemical reactions can be difficult to characterize. However, by considering elementary chemical reactions in the weld pool, the extent of simple equilibrium in the weld pool can be assessed. Although chemical equilibrium is not achieved in a weld pool, a trend toward equilibrium is generally observed that can be estimated using fundamental thermodynamic principles. Oxidation reactions in the weld pool can be described by the following generic reaction:

\[
xM + yO ⇔ M_xO_y
\]

(4)

According to the Law of Mass Action, the equilibrium constant, \( k \), for Equation 4 can be written as follows:

\[
k = \frac{[aM_x][O_y]}{[aM][aO]}
\]

(5)

where \([aM] \text{ and } [aO] \) are the activities of the weld metal alloying element, M, and oxygen, respectively, and \([aM_xO_y] \) is the activity of the metal-oxide inclusion in the weld metal. For equilibrium considerations, the activity of the metal-oxide can be taken as unity, which leads to the following relation:

\[
k = \frac{1}{[aM][aO]}
\]

(6)

This equation can be graphically represented for specific isothermal conditions as shown in Fig. 1. The shape of the curve is characteristic of an inverse product relationship and illustrates that as weld metal oxygen content increases, the alloy content in the weld metal will decrease. With knowledge of the oxidation reactions...
that will occur in the solidifying weld pool, it is possible to predict the direction toward which these reactions will go as changes are made in the welding flux. The results of these calculations can assist in the development of a specified final weld metal composition.

Competing chemical reactions within the weld pool will also affect the final weld metal chemical composition. As local concentrations of alloy elements vary with solidification (Refs. 50, 51), the local activity of alloying elements will change, altering the amount of alloying additions that will be oxidized. As a result, these competitive reactions will alter the predicted weld metal chemical composition.

One parameter to quantify the role of a flux in determining the final weld metal chemical composition is the “delta quantity.” The delta quantity for a specific alloying element is the amount of that element either gained or lost during the welding process and can be represented as:

\[ \text{[Delta Quantity]} = \text{[Analytic Content]} - \text{[Estimated Content]} \]  

Table 2 — Chemical Composition of the HSLA-100 Steel Plate and Core Rod Used in the Experiments

<table>
<thead>
<tr>
<th>Chemical Element</th>
<th>HSLA-100 Plate</th>
<th>ER100S-1 Rod</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon</td>
<td>0.06</td>
<td>0.064</td>
</tr>
<tr>
<td>Manganese</td>
<td>0.83</td>
<td>1.303</td>
</tr>
<tr>
<td>Phosphorus</td>
<td>0.011</td>
<td>0.006</td>
</tr>
<tr>
<td>Sulfur</td>
<td>0.002</td>
<td>0.006</td>
</tr>
<tr>
<td>Silicon</td>
<td>0.35</td>
<td>0.48</td>
</tr>
<tr>
<td>Copper</td>
<td>1.64</td>
<td>0.032</td>
</tr>
<tr>
<td>Nickel</td>
<td>3.43</td>
<td>2.043</td>
</tr>
<tr>
<td>Chromium</td>
<td>0.57</td>
<td>0.008</td>
</tr>
<tr>
<td>Molybdenum</td>
<td>0.62</td>
<td>0.502</td>
</tr>
<tr>
<td>Titanium</td>
<td>—</td>
<td>0.011</td>
</tr>
<tr>
<td>Aluminum</td>
<td>—</td>
<td>0.017</td>
</tr>
<tr>
<td>Zirconium</td>
<td>—</td>
<td>0.007</td>
</tr>
</tbody>
</table>

The estimated value for the chemical composition is determined by adding the contribution of elements from the welding wire to those of the contribution from the base plate by dilution calculation. The analytical content is that determined by the chemical analysis. A negative value of the delta quantity implies that the alloying element in consideration is lost to the slag and a positive value implies that the flux is contributing the alloying element in question to the weld pool. Zero delta quantity (null point) signifies no transfer of alloying elements from any of the sources. The most desirable flux systems are those that have delta quantities (at least for the major alloying elements) that remain relatively constant with variations in flux composition and welding condition. These fluxes allow for easy weld metal composition adjustment by adding or removing alloying elements from them. Additionally, the most stable flux systems are those fluxes that maintain the weld metal oxygen at low concentrations and thus minimize the deoxidation process.

Alloy additions can be made to the weld metal via the flux, and usually in the form of ferroalloys (e.g., Fe-Mn, Fe-Si, Fe-Ti, Fe-B, etc.). The use of ferroalloys in the welding flux for alloying is not ideal in the sense that the alloying element transfer to the weld metal may not be effective due to losses in slag-metal reactions or to the welding fume. Table 1 lists the commonly used ferro-additions with their expected element recovery in the weld deposit.

In this research, a methodology for the development of a SMA welding consumable for HSLA-100 steel was evaluated. Systematic changes were made to a rutile-based coating leading to a more basic electrode for this steel. Alloying elements, such as titanium and manganese, were introduced into the weld metal via ferro-additions. The synergistic effect of weld metal oxygen and weld metal alloy content on weld metal microstructure and properties was characterized to establish near-equilibrium trends for the deoxidation reactions that occur in the weld metal.

Experimental Procedure

Materials Used

The HSLA-100 steel welding coupons were 19.0 mm (3/4 in.) thick, and 101.6 by 152.4 mm (4 by 6 in.). The surface for welding was ground to remove any mill scale. Table 2 lists the chemical composition of the steel plate.

The steel core rod used in the consumables was an ER100S-1 (AWS A5.28-79) bare solid wire. The rod was 355.6 mm (14 in.) long and had a diameter of 3.2 mm (1/8 in.). The chemical composition for this rod is also shown in Table 2. The rod was chosen because of its commercial availability.

Welding Procedure

A constant current power source was used to produce welds using DCEP (direct current electrode positive). A constant arc voltage was maintained to the desired preset value by the use of a potential sensing device and a stepping motor that would either move the rod closer to the plate to decrease the voltage or increase the arc length to increase voltage. The welding parameters used for all the welds are shown in Table 3. The welding parameters were kept constant for all the welds to allow for more consistent evaluation of the effects of specific flux ingredients on the welding process. The heat input used was relatively high for the SMA welding process, but the instability found in some of the experimental electrodes could only be controlled at higher voltages. For this investigation, it is important to make variations in the flux components only, and that the parameters controlling heat input remain constant in order to understand the specific role of flux additions.

For microstructural analysis, single bead-on-plate welds were deposited in the flat position, without preheat. For Charpy impact testing, single bead-in-
the flat position, without preheat. For Charpy impact testing, single bead-in-
groove welds were produced. The grooves were 4 mm (0.16 in.) deep and
had an included angle of 60 deg. These welds were also deposited in the flat po-

tion, without preheat.

Flux Formulation Concept and Test Matrix

Figure 2 is a ternary representation of
the general changes in electrode coating
as the formulation progressed. The initial
electrodes had a high rutile and silica
content and their flux composition can
be located in the lower portion of the dia-
gram. As the changes were made in the
flux formulation, the silica and rutile
were replaced with more basic compo-
nents, which moved the coating com-
position toward the top portion of the
ternary diagram. Although CaCO₃ (CaO)
and CaF₂ are not expected to behave the
same, they are both considered to be the
primary constituents of a basic flux, and
are therefore grouped together in this fig-
ure. Following the arrow indicated in Fig.
2, an initial rutile-based electrode coat-
ing was modified to improve its metal-
lurgical characteristics in weld pool oxy-
gen and alloying elements control. The
changes were made gradually such that
the good electrode performance of a ru-
tile-based electrode would not be rad-
cially altered.

Electrode Formulation

An experimental matrix was devised
to systematically vary two components at
a time in the flux. The experimental elec-

trode designation has the format Axxx,
with x representing numbers from 0 to 9.
The first digit is the series number, the
second digit is the sequence number
within each series, and the third digit is
used to designate later modifications in
each series.

There are two methods of making
changes in electrode composition. The
first consists of changing the target com-
ponent, which decreases the overall
mass percent of the remaining compo-
nents, while maintaining the ratio among
them. The second approach requires
changing two components simultaneously (one decreasing a specific amount
while the other is increased by the same
amount).

In this research, the second approach
was used and changes in the coating
were made by direct replacement of one
component with another. A one-for-one
substitution maintains the weight percent
of the remaining flux components at a
constant, allowing for better determi-
 nation of the influence of the specific

<table>
<thead>
<tr>
<th>Component</th>
<th>Formulae</th>
<th>Primary Function</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alumina</td>
<td>Al₂O₃</td>
<td>Arc Stabilizer</td>
</tr>
<tr>
<td>Calcium Carbonate</td>
<td>CaCO₃</td>
<td>Shielding Gas</td>
</tr>
<tr>
<td>Calcium Fluoride</td>
<td>CaF₂</td>
<td>Slag Former</td>
</tr>
<tr>
<td>Feldspar</td>
<td>K₂O·Al₂O₃·6SiO₃</td>
<td>Shielding Gas</td>
</tr>
<tr>
<td>Ferromanganese</td>
<td>Fe-Mn</td>
<td>Deoxidizer</td>
</tr>
<tr>
<td>Ferrotitanium</td>
<td>Fe-Ti</td>
<td>Slag Former</td>
</tr>
<tr>
<td>Iron Oxide</td>
<td>Fe₂O₃</td>
<td>Slag Former</td>
</tr>
<tr>
<td>Kaolin</td>
<td>Al₂O₃·2SiO₃·H₂O</td>
<td>Slipping Agent</td>
</tr>
<tr>
<td>Mica</td>
<td>K₂O·3Al₂O₃·6SiO₃·H₂O</td>
<td>Slipping Agent</td>
</tr>
<tr>
<td>Potassium Silicate</td>
<td>K₂SiO₃</td>
<td>Binder</td>
</tr>
<tr>
<td>Potassium Titanate</td>
<td>2K₂O·2TiO₃</td>
<td>Arc Stabilizer</td>
</tr>
<tr>
<td>Silica</td>
<td>SiO₂</td>
<td>Slag Former</td>
</tr>
<tr>
<td>Sodium Silicate</td>
<td>Na₂SiO₃</td>
<td>Binder</td>
</tr>
<tr>
<td>Titanium Dioxide</td>
<td>TiO₂</td>
<td>Slag Former</td>
</tr>
</tbody>
</table>
Table 5 — Ferromanganese Additions, Weld Metal Manganese Content, and Manganese Delta Quantity for the A5xx Welding Electrodes

<table>
<thead>
<tr>
<th>A5xx Welding Electrode</th>
<th>Ferromanganese Addition (wt-%)</th>
<th>Weld Metal Manganese Content (wt-%)</th>
<th>Manganese Delta Quantity (wt-%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A420</td>
<td>2.2</td>
<td>0.26</td>
<td>-0.79</td>
</tr>
<tr>
<td>A510</td>
<td>4.2</td>
<td>0.39</td>
<td>-0.68</td>
</tr>
<tr>
<td>A520</td>
<td>6.2</td>
<td>0.64</td>
<td>-0.45</td>
</tr>
<tr>
<td>A530</td>
<td>8.2</td>
<td>0.83</td>
<td>-0.24</td>
</tr>
</tbody>
</table>

changes made. All electrodes within each series were evaluated and the one that produced the best results for the flux system analyzed was used as the starting formulation for the next series. Considering Table 4, each substitution was made with the primary function of each component in mind. Nevertheless, careful considerations that each change would have an influence on the metallurgical properties of the resultant weldment, in the form of weld metal chemical composition and microstructure, were also made.

Figure 3 shows the electrode “genealogy” for the entire test matrix. The major constituents changed are placed at the start of each line, and the electrode selected as the starting point for the next series appears highlighted (circled by a bold circle) along the series line. These electrodes are the primary electrodes. For example, in the A2xx series, CaF2 was added to gradually replace Al2O3. Electrode A230 performed most satisfactorily in the series and was chosen to be further modified in the A3xx series. The overall consideration in the modification of the welding flux was to characterize the significant changes in the behavior of the welding electrode as the coating was adjusted from rutile to more basic in nature.

Methodology of Formulation

The first electrode (A1) was formulated from an experimental rutile-based electrode, developed prior to this investigation (Ref. 53). Its composition was chosen because of its good welding performance such as slag formability, slag detachability, arc stability, and weld bead morphology.

The initial electrode series was designated A1xx. These electrodes had high rutile content and were comparable to a commercial E6013 steel welding electrode. Systematic additions of FeTi were made in this coating to study the influence of titanium on the microstructure in an electrode with high oxygen potential. Ferro-boron was removed from the electrode at this point, with the intention of adding it back into the system in a later series. However, the idea of reintroducing ferro-boron was eventually abandoned.

The A2xx series was characterized by the replacement of TiO2 with Al2O3, with alumina increasing from 2.8 to 22.2 wt-%. Alumina is amphoteric and should reduce the oxygen in the weld metal while decreasing the viscosity of the slag. This step was the first in a series of alterations to the oxygen potential of the electrode to characterize the effect of oxygen on weld metal microstructure.

For the A3xx series, the alumina was removed and substituted with CaF2. This procedure was done to further reduce the oxygen in the weld metal, as well as decrease the viscosity of the slag. It is also suggested (Ref. 54) that calcium fluoride reduces the free hydrogen in the weld metal by the reaction:
welding. Alumina is an amphoteric ingredient that alters the amount of oxygen pickup in the weld metal. However, the effect of alumina will depend on the other ingredients present in the slag. If these ingredients are more basic than alumina, the weld pool will pick up oxygen from the dissociation of alumina. If the other ingredients are more acid than alumina, then alumina will behave as a basic oxide limiting the amount of oxygen pickup in the weld pool. The reduction of ferric oxide would also lead to a decrease in the weld metal oxygen content.

Both K₂SiO₃ and Na₂SiO₃, individually and mixed, were used as a binder. They did not affect to any measurable degree the performance of the experimental electrodes. The electrodes that contained sodium silicate produced welds that exhibited a slightly lower diffusible hydrogen content, around 7.5 ml/100g weld metal. On the other hand, the electrodes extruded with the mixed binder generated welds that had diffusible hydrogen as high as 8.5 ml/100g weld metal. For more specific information on the minor ingredients of the flux coating, please refer to Refs. 53 and 56.

**Metallography**

Quantitative metallography was done for the weld metals deposited with the Al1xx, A6xx, and A9xx series electrodes. Point counting technique according to IIW Standard IIW-IX-153388 was used. One hundred points were counted on ten separate fields at a magnification of 800X.

The microstructure was characterized by five separate phases. Each of these phases is distinct in morphology and their proportional contents are indicative of different properties of the weld metal. A brief discussion of their morphology is given below.

1) Primary Ferrite (PF). Ferrite that forms along the prior austenite grain boundaries and blocks of intragranular ferrite that contain no second phase.

2) Acicular Ferrite (AC). Small non-aligned ferrite laths (aspect ratio less than 4 to 1) that form within the prior austenite grains.

3) Ferrite with Aligned Second Phase (FS/Al). Long needle-like, parallel ferrite laths (aspect ratio greater than 4 to 1) with carbides in between laths. These microstructural features can also be classified as either Widmanstätten ferrite or upper bainite.

4) Ferrite with Second Phase Non-Aligned (FS/NA). Ferrite that surrounds acicular ferrite or other random microphases. These microstructural features resemble somewhat the lower bainite as defined in the steel metallurgy literature.

5) Martensite (M). Colonies of needle-like ferrite that are larger than adjacent ferrite laths within prior austenite grains.

**Chemical Analysis**

The chemical analysis of the welds was carried out using an ARL optical emission spectrometer. The reinforcement was removed from the weld bead, leaving a flat surface required for analysis. Determinations were performed on three locations on each sample and the average of these measurements was used.

Weld metal oxygen content data was obtained using a Leco TC-136 analyzer. The weld metal was removed from the base plate and cut into one-gram samples. Four samples were used from each weldment, and the average was taken to determine the weld metal oxygen content.

**Charpy V-Notch Impact Toughness Test**

All-weld-metal subsized specimens were prepared (2.5 by 5.0 by 55.0 mm) according to ASTM Standard E23 (1991). The Charpy specimens were tested at -60°C (-76°F) and a minimum of three specimens from each of the A6xx welds was tested.

**Hardness and Strength Measurements**

Rockwell C hardness measurements were conducted on the Leco motorized digital Rockwell hardness tester (Model R-600). The weld bead was ground flush with the base plate and measurements (in the form of hardness profiles) were taken transverse to the longitudinal axis of the weld bead, as well as along the longitudinal axis. These values were then averaged to give a value for the hardness of the weldment. Strength correlations were drawn from these measurements using conversion algorithms proposed by Cahn et al. (Ref. 55). These algorithms were used because of the lack of other such expressions devised specifically for weldments. However, the application of this conversion methodology is not expected to result in gross estimate errors.

**Results and Discussion**

**Weld Metal Oxygen and Alloy Content**

The discussion of weld metal alloy content and weld metal oxygen content will be presented collectively, as the effect of one on the other is of primary importance in the development of weld metal properties. Characteristics of the effect of weld metal oxygen content on the alloy content will be discussed in relation to the Law of Mass Action — Fig. 1. Competitive reactions between alloying elements and oxygen are also considered as to the role that these interactions have on the final outcome of the weld metal alloy and inclusion content.

The weld metal oxygen content as a function of basicity index of welding electrode for the primary electrodes is shown in Fig. 4. As was expected and desired, with the exception of the weld metal oxygen content for the A420 welding electrode, there was a successive decrease in oxygen as the electrodes were formulated. The A420 welding electrode had a high ferric oxide content and was expected to increase the weld metal oxygen content.

The decrease in weld metal oxygen was intended to be from the high-oxygen regime (greater than 600 ppm of weld metal oxygen) to the low-oxygen regime (less than 300 ppm of weld metal oxygen) according to the range proposed by Anson, et al. (Ref. 5). All welds prepared using the Al1xx series electrodes had weld metal oxygen content greater than 600 ppm, and the final electrodes, the A9xx series, deposited weld metal with oxygen content of approximately 300 ppm.
A review of the corresponding microstructures is done in a later section.

Figure 5 shows the plot of weld metal titanium as a function of weld metal oxygen resulting from selected electrodes. These were the "primary electrodes" from which the families of experimental electrodes were generated. The shape of the curve indicates an inverse product relation, as suggested by thermodynamics, implying that the initial suggestion of thermodynamic equilibrium trends in the weld metal was correct. This correlation attests the direct effect of deoxidation in the weld deposit. Increasing the weld metal oxygen content decreased the amount of weld metal deoxidizers and hardenability agents. Similar behaviors were observed for silicon and manganese.

Using what is known of the behavior of specific flux ingredients, the weld metal chemical content can be adjusted to yield the desired result. As an example, consider that for a given application it is desired to have a titanium content of 200 ppm. Figure 5 shows that for the particular types of electrodes used in this investigation, the oxygen level in the weldment will be in the region of 300 to 500 ppm. In case that titanium must be removed from the weld metal, an electrode that would result in over 600 ppm of oxygen would be needed.

Discrepancies of results of weld metal alloy content as a function of the weld metal oxygen content could partially be due to competitive reactions occurring in the weld pool. Three examples of these reactions are:

\[
\begin{align*}
\text{Si} + 2\text{MnO} & \leftrightarrow \text{SiO}_2 + 2\text{Mn} \\
\text{Ti} + 2\text{MnO} & \leftrightarrow \text{TiO}_2 + 2\text{Mn} \\
\text{SiO}_2 + \text{Ti} & \leftrightarrow \text{Si} + \text{TiO}_2
\end{align*}
\]

for which the Law of Mass Action can be described as:

\[
\begin{align*}
k_9 &= \frac{[\text{SiO}_2][2\text{Mn}]}{[\text{Si}][2\text{MnO}]} \\
k_{10} &= \frac{[\text{TiO}_2][2\text{Mn}]}{[\text{Ti}][2\text{MnO}]} \\
k_{11} &= \frac{[\text{Si}][\text{TiO}_2]}{[\text{SiO}_2][\text{Ti}]} \tag{14}
\end{align*}
\]

Where \(k_9, k_{10}\), and \(k_{11}\) are the equilibrium constants for the reactions represented in Equations 9, 10, and 11, respectively. The graph of each of the respective functions is shown in Fig. 6. The activity of the oxides is taken to be unity, and the activity of the elemental form of each of the al-
loy, in this situation, is equated to the respective concentration. It should be understood that the use of these concentrations does not imply that equilibrium has been achieved, but instead allows for the determination of the extent that the reactions are going toward equilibrium. For each of the reactions, a linear correlation is shown between the competitive reactions that are present in the weld metal with the slope of the graph corresponding to an apparent equilibrium constant for the reactions. With these competitive reactions taking place, an expected widening of the plot of the equilibrium behavior of the weld metal alloy content and the weld metal oxygen content is observed. The increase in activity of one of the elements will affect the activity of a second component and change the reactivity of that element in the weld pool.

**Delta Quantity**

A flux coating may also be characterized by the effect that it has on the alloying of the weldment. The way in which a flux system will alter the chemical content of the weld metal will be indicative of the reactivity of the elements in the system.

Graphs of the weld metal delta quantity as a function of weld metal oxygen content for manganese, silicon and titanium, respectively, are shown in Fig. 7. For the three elements considered, the rutile electrode (e.g., A100 electrodes) led to the greatest loss of alloying elements to the slag, represented by the negative delta quantity. This effect is due to the abundance of oxygen in the weld pool. As the amount of oxygen in the weld metal decreased, the delta quantities were found to go to zero ("null point"), implying that the flux coating in the more basic electrodes (e.g., A530 and A610 electrodes) removed less of the elements from the weld metal.

In the A5xx series, ferro-manganese was added to the flux to increase the weld metal manganese to a level comparable to that of the electrode core wire. The weld metal manganese content, delta quantity, and ferro-manganese additions are shown in Table 5 for the A5xx series. As expected, the addition of ferro-manganese to the flux coating led to an increase in the weld metal manganese content.

In the A1xx and A6xx series electrodes, ferro-titanium was added to the coating. As was done for the A5xx electrodes, the ferro-titanium additions, weld metal titanium content, and delta quantity are listed in Table 6. As expected, the addition of ferro-titanium to the flux led to an increase in the weld metal titanium content. This effect is further enhanced by the removal of hematite from the coating, as ferro-titanium is added. The removal of hematite in series A5xx electrodes decreased the weld metal oxygen, which also resulted in less removal of alloying elements. In contrast, the delta quantity in the A1xx series electrodes was less evident as ferro-titanium additions were made. This observation implies that a weld metal deposited with a rutile electrode will have small variations in the weld metal alloy content as ferroalloy additions are made. However, lower oxygen levels found in the welds deposited by the more basic electrodes, as shown in Fig. 5, will directly result in the larger variations in alloy content.

An important consideration in the addition of ferroalloys in fluxes is the recovery of the elements. The recovery of elements can be determined by plotting weld metal alloy content as a function of alloy component additions in the flux. Figure 8 shows a plot of the weld metal titanium content as a function of the ferro-titanium additions to the flux for the A1xx and A6xx series electrodes. The more basic electrode (A6xx series) presented better recovery of titanium than the rutile electrodes, demonstrated by the slopes of the two lines. At 4.0 wt-% of ferro-titanium addition, for example, approximately 200 ppm of titanium was recovered in the weld metal with the more basic electrode, while only approximately 80 ppm was recovered with the rutile electrode.

As illustrated in Fig. 7B, the silicon delta quantity as a function of oxygen is a better demonstration of the effect of the flux coating on weld metal alloy content, since silicon was not added to the flux in the form of ferro-additions. As the oxygen in the weld metal decreases, the silicon delta quantity approaches zero, which indicates the presence of a null point in the system.

In general, the delta quantity for the alloying elements of the weld metal approached zero as the oxygen content was decreased. This finding allows for the initial selection of the electrode core rod. However, realizing that the data developed were for single-pass bead-on-plate welds, the alloy content of the weld metal determined may not yield the best microstructure for multiple pass welding. Therefore, further optimization of the weld metal alloy content that takes into consideration the final weld metal prop-

**Fig. 7 — Weld metal delta quantity at A — manganese; B — silicon; C — titanium as a function of weld metal oxygen content for selected electrodes.**
Table 7 — Results of Point Count for the Welds Deposited With the A1xx, A6xx, and A9xx Series Electrodes (in vol-%)

<table>
<thead>
<tr>
<th>Electrode Designation</th>
<th>PF</th>
<th>AF</th>
<th>FS(A)</th>
<th>FS(NA)</th>
<th>M</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1</td>
<td>12</td>
<td>18</td>
<td>33</td>
<td>37</td>
<td>37</td>
</tr>
<tr>
<td>A100</td>
<td>28</td>
<td></td>
<td>54</td>
<td></td>
<td>18</td>
</tr>
<tr>
<td>A110</td>
<td>18</td>
<td>12</td>
<td>49</td>
<td>21</td>
<td>43</td>
</tr>
<tr>
<td>A120</td>
<td>15</td>
<td>6</td>
<td>36</td>
<td>43</td>
<td>21</td>
</tr>
<tr>
<td>A130</td>
<td>16</td>
<td>14</td>
<td>47</td>
<td>23</td>
<td>21</td>
</tr>
<tr>
<td>A140</td>
<td>15</td>
<td>24</td>
<td>40</td>
<td>21</td>
<td>31</td>
</tr>
<tr>
<td>A610</td>
<td>1</td>
<td>59</td>
<td>9</td>
<td></td>
<td>31</td>
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<tr>
<td>A620</td>
<td>3</td>
<td>57</td>
<td></td>
<td></td>
<td>40</td>
</tr>
<tr>
<td>A630</td>
<td>3</td>
<td>57</td>
<td></td>
<td></td>
<td>40</td>
</tr>
<tr>
<td>A640</td>
<td></td>
<td></td>
<td></td>
<td>31</td>
<td>60</td>
</tr>
<tr>
<td>A910</td>
<td></td>
<td>54</td>
<td>12</td>
<td>6</td>
<td>28</td>
</tr>
<tr>
<td>A920</td>
<td></td>
<td>44</td>
<td>13</td>
<td>3</td>
<td>40</td>
</tr>
<tr>
<td>A930</td>
<td></td>
<td>26</td>
<td>7</td>
<td></td>
<td>67</td>
</tr>
</tbody>
</table>

Table 7 lists the results of point counting for the welds deposited with the A1xx, A6xx, and A9xx series electrodes. Micrographs (800X magnification) of the weld metals deposited by the A100, A610, and A910 welding electrodes are shown in Fig. 9.

The largest difference in the point counting results was seen between the A1xx electrodes and the A6xx electrodes. Flux coating composition adjustment will allow for the fine tuning of the final weld metal composition and the final selection of the core rod used in the SMA welding process.

Microstructure

Addition of ferro-titanium at these two stages of the formulation process allowed for comparison of the effect of a rutile and a more basic electrode on the weld metal composition and the weld metal microstructures. In both instances, the titanium content of the weld metal was altered by ferro-titanium additions, and as discussed earlier, the addition of ferro-titanium is expected to lead to an increase in the amount of acicular ferrite in the weld metal. However, weldments made with the A6xx series electrode (Fe-Ti: from 0.0 to 3.0 wt-%) showed microstructures that predominately exhibited grain boundary and sideplate ferrite. Conversely, weldments made with the A1xx series electrode (Fe-Ti: from 0.0 to 3.0 wt-%) showed microstructures that predominately exhibited grain boundary and acicular ferrite.

In the Fe-Ti range of 0.0 to 3.0 wt-%, the A9xx series presented a dual-phase microstructure as the A6xx series and the A1xx series. However, the A9xx series weld metals exhibited longer ferrite needles, suggesting that the FS phase likely formed at the expense of acicular ferrite.

In general, grain refining in the weld metal was observed as the electrodes moved from rutile to more basic in nature. The first electrodes deposited weld metal that was high in proeutectoid ferrite and sideplate ferrite. As the weld metal was refined, phases that were characterized by small interlocking needles (acicular ferrite) tended to predominate, which led to better mechanical properties.

Hardness and Strength

Hardness was measured for all the
welds. As indicated earlier, specific additions in the A1xx, A5xx, and A6xx series electrodes were made to determine the effect of several alloying elements on the hardenability of the weld metal. Table 8 lists the hardness values (HRc) and Pcm for the welds deposited by these electrodes. The measured hardness varied dramatically for the A6xx series electrodes in spite of the fact that the Pcm values were relatively close. For these higher values of Pcm it is expected that the weld metal would exhibit high hardness, as seen in the A640 electrode. However, for the A610 and A620 electrodes, the hardness is lower than expected. This result suggests that titanium at the levels found in these electrodes is advantageous to the formation of acicular ferrite in the weld metal. On the other hand, the ineffectiveness of the low titanium content present in the A1xx series electrodes (less than 100 ppm) may suggest that in a high-oxygen environment, titanium is ineffective in altering the phase transformation behavior in the weld metal, with grain boundary and sideplate ferrite dominating the microstructure.

To further illustrate the effect of chemical composition on the hardness, Fig. 10 shows the measured weld metal hardness as a function of the Pcm values. With the transition from the A5xx and A6xx electrodes there is an increase in the Pcm value for the weld metals, although there is no change in the hardness. This result is different than for the rest of the welds, where a constant increase in hardness can be seen with the increase in the Pcm. The lack of a term in the Pcm expression for titanium, which even in small amounts has a significant affect on the weld metal microstructure, results in the discrepancy of the data with predicted results.

The addition of titanium to the weld metal promotes the formation of acicular ferrite, which is a softer phase than martensite and bainite (predominant microstructure in the A5xx weldments). Therefore, titanium is effective in A610 and A620 welds with concentration between 150 to 250 ppm. With further increase in titanium in as in the welds made using the A640 electrodes, hardenability effect predominates, with the observation of increasing martensite, F5 phase and hardness.

Tensile and yield strength data were estimated from the hardness data using the conversion algorithms proposed by Cahoon, et al. (Ref. 55). The results of these conversions are listed in Table 9 for the welds deposited with the A6xx electrodes and the A9xx electrodes. The HRc values are also listed for reference. The desired yield strength for the weld metal is between 115 and 120 ksi (assuming 15 to 20% strength overmatching with respect to the base metal). The weld metal deposited by the A610, A620, and A630 welding electrodes falls within this category. Again, this optimization is due to the fact that the microstructure optimizes both the strength and toughness of the weld metal. The 2:1 ratio of acicular ferrite to martensite augments the mechanical properties of the weld metal.

**Toughness**

Charpy V-notch data were obtained for the A6xx series electrodes, and the energy absorbed at -60°C as a function of weld metal titanium content is illustrated in Fig.

---

**Table 8 — Calculated Pcm Values for Designated Welds With Hardness Data**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Pcm</th>
<th>Hardness (HRc)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1</td>
<td>0.173</td>
<td>24</td>
</tr>
<tr>
<td>A100</td>
<td>0.176</td>
<td>22</td>
</tr>
<tr>
<td>A110</td>
<td>0.178</td>
<td>23</td>
</tr>
<tr>
<td>A120</td>
<td>0.176</td>
<td>25</td>
</tr>
<tr>
<td>A130</td>
<td>0.176</td>
<td>24</td>
</tr>
<tr>
<td>A140</td>
<td>0.177</td>
<td>26</td>
</tr>
<tr>
<td>A6010</td>
<td>0.235</td>
<td>32</td>
</tr>
<tr>
<td>A620</td>
<td>0.253</td>
<td>31</td>
</tr>
<tr>
<td>A630</td>
<td>0.261</td>
<td>34</td>
</tr>
<tr>
<td>A640</td>
<td>0.280</td>
<td>39</td>
</tr>
</tbody>
</table>

**Table 9 — Tabulation of the Estimated Tensile and Yield Strengths for the Welds Deposited with the A6xx and A9xx Welding Electrodes**

<table>
<thead>
<tr>
<th>Electrode Designation</th>
<th>Hardness (HRc)</th>
<th>Tensile Strength (MPa/ksi)</th>
<th>Yield Strength (MPa/ksi)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A610</td>
<td>32</td>
<td>1020/150</td>
<td>820/120</td>
</tr>
<tr>
<td>A620</td>
<td>31</td>
<td>990/140</td>
<td>800/120</td>
</tr>
<tr>
<td>A630</td>
<td>34</td>
<td>1060/150</td>
<td>850/120</td>
</tr>
<tr>
<td>A640</td>
<td>39</td>
<td>1120/160</td>
<td>980/140</td>
</tr>
<tr>
<td>A910</td>
<td>35</td>
<td>1080/160</td>
<td>870/130</td>
</tr>
<tr>
<td>A920</td>
<td>37</td>
<td>1150/170</td>
<td>920/130</td>
</tr>
<tr>
<td>A930</td>
<td>42</td>
<td>1180/170</td>
<td>1070/150</td>
</tr>
</tbody>
</table>

---

**Fig. 10 — Plot of Pcm as a function of weld metal hardness for the HSLA-100 steel welds.**

**Fig. 11 — Plot of the Charpy impact energy as a function of weld metal titanium content for the welds deposited with the A6xx series electrodes.**
11. It can be observed that, despite the use of sub sized CVN specimens, a distinct fracture behavior could be observed for the welds. Optimal toughness was found when the titanium level was 150 ppm. A slight increase in the weld metal titanium content was found to significantly decrease the impact toughness at -60°C. This behavior indicates that after a certain level of addition, titanium was disadvantageous in the weld metal and the transition temperature for the impact specimens increased.

The weld metal that exhibited the highest toughness (A610) was found to be associated with an increase in the acicular ferrite content of the weld metal. The weld metal that produced the highest toughness was an essentially dual-phase microstructure that was mainly acicular ferrite (60 vol-%) and martensite (30 vol-%). The low-impact toughness of Weld A630 and A640 can be attributed to the increased amounts of martensite, 

The extensive SMA welding electrode coating investigation conducted in this work has led to an understanding of the formation of electrodes for HSLA-100 steels. The conclusions drawn from the results of this work are as follows:

1) A methodology was established to study flux coating formulations in which the basicity index of the flux was progressively changed from rutile to more basic in nature. Specific alterations in the system allowed for the characterization of individual effects of the components on both the welding flux function as well as the weld metal chemical composition.

2) An understanding of the equilibrium type relationships that occur in the weld metal during solidification and slag formation lead to a knowledge of the controlling reactions (Mn-O, Si-O, and Ti-O) in determining the final weld metal chemical composition.

3) A base flux formulation was established that will deposit a weld metal with desirable mechanical properties. This electrode was more basic in nature (when compared with a rutile electrode) and used ferro-manganese and ferro-titanium additions to control the weld metal oxygen content. This composition led to the reduction of grain boundary and side plate ferrite and promoted the formation of acicular ferrite, bainite and martensite.

4) A microstructure that was mainly acicular ferrite (60 vol-%) and martensite (30 vol-%) was found to exhibit good strength and acceptable toughness in single-pass HSLA-100 steel weldments. This microstructure resulted from the interaction of specific amounts of alloying elements (Mn, Si and Ti) with weld metal oxygen.

Acknowledgment

The authors acknowledge and appreciate the financial support of the SP-7 welding panel of the National Shipbuilding Research Program.

References

Summary of the relation between the microstructure of weld metal and its properties, particularly in the context of C-Mn steels and high-strength steels. The microstructure is influenced by various factors such as the choice of welding process, welding parameters, and the chemistry of the weld metal. The effects of titanium and boron additions on the microstructure and properties of weld metal are also discussed. The role of inclusions, especially non-metallic inclusions, in controlling the phase transformations and properties of weld metal is highlighted. The emphasis is on the development of weld metal compositions and processes that can optimize microstructure and properties for specific applications.