Stepwise Methodology of Welding Flux Formulation:

From Rutile Grade to CaO-CaF$_2$ Grade

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Abstract

In this research, a stepwise flux-design methodology was tested using shielded metal arc (SMA) welding on HSLA-100 steel. Systematic changes were made to a rutile-based flux coating to result in a more "basic" electrode for this steel. The changes involved in replacing the initial high silica and rutile content with components such as CaCO$_3$, i.e. CaO, and CaF$_2$. Other flux ingredients such as Al$_2$O$_3$, Fe-Ti, and Fe$_2$O$_3$ were also systematically introduced. The changes were gradual such that the good electrode performance of a rutile-based electrode would not be radically altered.

The flux composition changes were made by varying the concentration of two components simultaneously, partially replacing one component with another. A one-for-one substitution maintains the weight percent of the remaining flux components at a constant.

The reference electrode (Al) was formulated from an experimental rutile-based electrode. This electrode was chosen because of its excellent welding performance regarding slag formability, slag detachability, arc stability, and weld bead morphology.

The first experimental electrode series was designated A1xx, with small adjustments of Fe-Ti additions in the reference electrode. The A2xx series resulted from A1xx series by the replacement of TiO$_2$ with Al$_2$O$_3$. For the A3xx series, Al$_2$O$_3$ was substituted with CaF$_2$. The A4xx series involved the substitution of rutile with ferric oxide (Fe$_2$O$_3$). In A5xx series, Fe-Mn was added at the expense of Fe$_2$O$_3$. To further reduce ferric oxide, Fe-Ti was added to the coatings in the A6xx series. For the A7xx series, mica and kaolin, both containing water of crystallization, were removed and replaced with their primary oxides. Finally, the CaF$_2$/CaCO$_3$ ratio was adjusted in the A8xx series.

Some additions exercised control on slag oxygen potential, weld metal hardenability and microstructure. Other additions influenced the electrode performance, arc stability, and slag behavior. The research program was successful in formulating a flux coating that exhibited good electrode performance and provided good weld metallurgical characteristics.

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INTRODUCTION

To achieve successful shielded metal arc (SMA) welds of HSLA-100 steel with properties comparable to those of the base plate, consumables with excellent properties are required. The electrode must produce weld metal with proper composition and microstructure to give both sufficient strength and toughness. Thus, it is essential to know the oxygen transfer behavior between the electrode and weld metal. The low solubility of oxygen in α-iron suggests that the oxygen detected in the weld metal must exist in the form of inclusions [1]. A majority of these inclusions forms as a result of different deoxidation steps in the liquid weld pool, with the final inclusions forming interdendritically during solidification [2,3]. It is these inclusions that affect the formation of weld metal ferrite during austenite decomposition.

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, titanates, ... , and affect subsequent solid-state transformations [2]. Since these deoxidation reactions will occur rapidly due to the high temperatures and large interfacial areas available for reaction [4,5], therefore, an understanding of the mechanisms that control weld metal oxygen is essential to the formulation of electrodes.

Alloying elements in the weld metal play a significant role in defining the final microstructural phases present. They strengthen the weld metal through solid solution or precipitation strengthening [6]. In addition to hardenability, they can also react with oxygen to form inclusions that serve as nucleation sites for ferrite. 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. The individual effect is sometimes difficult to determine due to the synergistic effects with 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, galaxite ($MnO.Al_2O_3$), which acts as nucleation sites for acicular ferrite [7,8]. 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 toughness. Therefore, the level of manganese within a given flux system must be adjusted to achieve optimal properties.

Titanium and boron have also been reported to improve the mechanical properties of weld metals [9-14]. 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 [15-20]. 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.

Weld Pool Pyrometallurgy

The final weld metal chemical composition is determined by the slag-metal reactions that occur in the weld pool [2,21-24]. However, 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. 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 [25,26], 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 welding process and can be represented as:

$$\begin{bmatrix} Delta \\ Quantity \end{bmatrix} = \begin{bmatrix} Analytical \\ Content \end{bmatrix} - \begin{bmatrix} Estimated \\ Content \end{bmatrix} \qquad (1)$$

The estimated value for the chemical composition is determined by adding the contribution of elements from the welding consumable 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 minimizing 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 alloying element transfer to the weld metal may not be effective due to losses in slag-metal reactions or to the welding fume.

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 (than the original rutile electrode) for this steel. Alloying elements, such as titanium and manganese, were introduced into the weld metal via ferro-additions.

EXPERIMENTAL PROCEDURE

Typical HSLA-100 steel welding coupons were used. The steel core rod used in the experimental consumables was an AWS ER100S-1 bare solid wire that matched well the base plate composition. An automatic voltage controller was used to maintain constant the arc length. The welding parameters were also kept constant for all the welds to allow for more consistent evaluation of the effects of specific flux ingredients on the welding process.

Flux Formulation Concept and Test Matrix

Figure 1 is a ternary representation of the general changes in electrode coating as the formulation evolved. The initial electrodes had a high rutile and silica content with their flux

composition located in the lower portion of the diagram. As changes were made in the flux formulation, the silica and rutile were replaced with more basic components, which moved the coating composition towards the top portion of the ternary diagram. Although $CaCO_3$ (CaO) and CaF_2 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 figure. Following the arrow indicated in Figure 1, an initial rutile-based electrode coating was modified to improve its metallurgical characteristics in weld pool oxygen and alloying element control. The changes were made gradually such that the good electrode performance of a rutile-based electrode would not be radically altered.
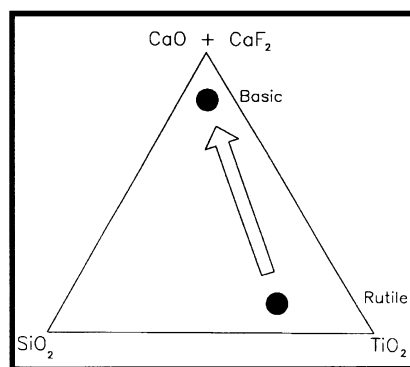

Figure 1. Schematic Diagram of the Formulation Concept: shifting from a rutile-base flux, rich in TiO_2 and SiO_2, to a basic flux that is rich in CaO and CaF_2.

Electrode Formulation

An experimental matrix was devised to systematically vary two components at a time in the flux. The experimental electrode designation has the following format:

Axxx

with "*x*" representing numbers from 0 to 9. The first digit is the series number, the second and third digits are the sequence number within each series, designating modifications to the formulation. Changes in the coating were made by direct replacement of one component with another. A one for one substitution maintains constant the weight percent of the remaining flux components, allowing for better determination of the influence of the specific 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 I, 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.

Table I. Flux Components and Their Primary Functions.

Component	Chemical Formula	Primary Function
Alumina	Al_2O_3	Arc Stabilizer
Calcium Carbonate	$CaCO_3$	Shielding Gas
Calcium Fluoride	CaF_2	Slag Former
Feldspar	$K_2O.Al_2O_3.6SiO_2$	Slag Former
Ferro-boron	Fe-B	Alloying
Ferro-manganese	Fe-Mn	Deoxidation-Alloying
Ferro-titanium	Fe-Ti	Deoxidation-Alloying
Iron Oxide	Fe_2O_3	Slag Former
Kaolin	$Al_2O_3.2SiO_2.H_2O$	Slipping Agent
Mica	$K_2O.3Al_2O_3.6SiO_2.H_2O$	Slipping Agent
Potassium Silicate	$K_2O.SiO_2$	Binder
Potassium Titanate	$K_2O.TiO_2$	Arc Stabilizer
Silica	SiO_2	Slag Former
Sodium Silicate	$Na_2O.SiO_2$	Binder
Titanium Dioxide	TiO_2	Slag Former

Figure 2 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, CaF_2 was added to gradually replace Al_2O_3. Electrode A230 performed most satisfactorily in the series and was chosen to generate the A3xx series. The overall considerations 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 [27]. Its composition was chosen because of its good

welding performance such as slag formability, slag detachability, arc stability, and weld bead morphology.
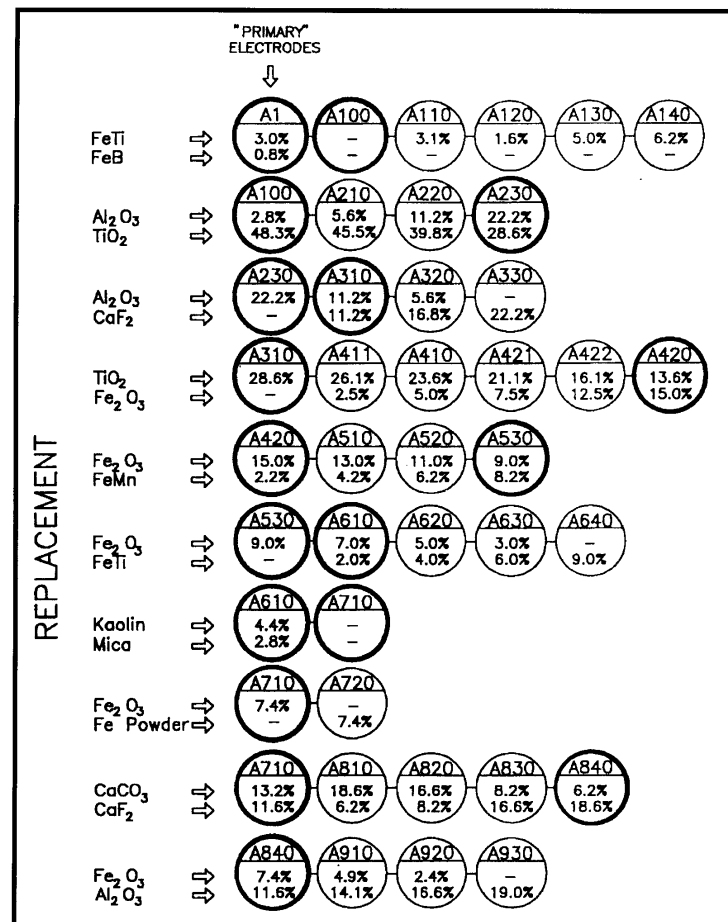

Figure 2. Schematic Representation of the Electrode Formulation Sequence.
Each Series provided a Starting Composition for the Next Series.

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 Fe-Ti 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.

The A2xx series was characterized by the replacement of TiO_2 with Al_2O_3, with alumina increasing from 2.8 to 22.2 wt. pct. 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 CaF_2. 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 [28] that calcium fluoride reduces the free hydrogen in the weld metal by the reaction:

$$CaF_2 + H_2O \Leftrightarrow CaO + 2HF \qquad (2)$$
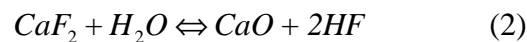
Despite the desirable properties of CaF_2, high contents of this ingredient in the flux formulation causes arc instability during welding, requiring extremely high mean voltage to sustain the arc. It also decreases the viscosity of the molten slag reducing the weld pool coverage.

The A4xx series involved the substitution of rutile with ferric oxide (Fe_2O_3). This substitution resulted in a further increase of the basicity index and improved arc stability, although there was a subsequent increase in the weld metal oxygen. Part of the hematite would be removed in subsequent steps with the substitution of ferroalloys.

The A5xx series consisted of additions of Fe-Mn at the expense of Fe_2O_3. The manganese content in the weld metal was increased at this point in an effort to increase the hardenability of the weld metal, depressing the ferrite start temperature to promote lower transformation temperature products. The lowering of the austenite decomposition temperature occurred also as a result of the decrease in oxygen and oxide inclusions.

Addition of Fe-Ti to the coating was made in the A6xx series. Ferric oxide was further reduced at this point. Titanium was added to promote the formation of acicular ferrite in the weld metal with the formation of titanium oxides in the weld metal. Also, comparison of the recovery of titanium in this series (more basic in nature), could be made with the initial ferro-titanium additions in the A1xx series (rutile in nature).

For the A7xx series, mica and kaolin, both containing water of crystallization, were removed. This removal was done in an attempt to verify the importance of chemically bonded water on oxygen generation in the weld metal. Also, ferric oxide was replaced with iron powder in an effort to further decrease oxygen.

The CaF_2 to $CaCO_3$ ratio was altered in the A8xx series. Control of the weld metal oxygen as well as slag viscosity was the goal of this alteration. Calcium fluoride is known

from steelmaking to reduce the melting temperature of the slag and thus lowering the viscosity. $CaCO_3$ decomposes in the arc resulting in the formation of CO_2 gas and CaO. Carbon dioxide will serve to shield the weld pool while CaO, incorporated in the slag, will affect the melting temperature and viscosity of the slag, and the amount of oxygen in the weld metal.

In the final series, A9xx, ferric oxide was replaced with alumina in an effort to improve slag viscosity for out-of-position welding. However, the effect of alumina will depend on the other ingredients present in the slag. If these ingredients are more basic than alumina, then 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 K_2SiO_3 and Na_2SiO_3, individually and mixed, were used as 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 diffusbile hydrogen as high as 8.5 ml/100g weld metal.

RESULTS AND DISCUSSION

Weld Metal Oxygen and Alloy Content

With the exception of 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 Abson et al [29]. Accordingly, all welds prepared using the A1xx series electrodes had weld metal oxygen content greater than 600 ppm, and the final electrodes, the A9xx series, deposited weld metals with oxygen content of approximately 300 ppm.

Figure 3 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, attesting 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.
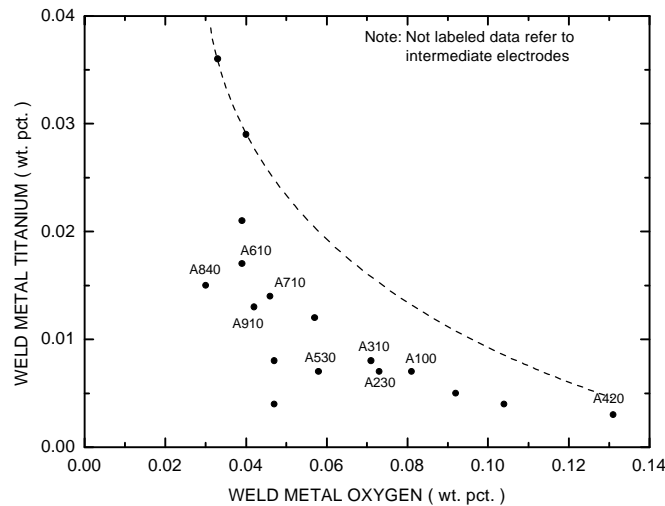

Figure 3. Weld Metal Titanium Content as a Function of Weld Metal Oxygen Content.

Delta Quantity

A graph of the weld metal delta quantity as a function of weld metal oxygen content for manganese, silicon and titanium are shown in Figure 4, respectively. For the three elements considered, the rutile electrode (e.g. A100 electrode) 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 II 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 can be seen in Table III, 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
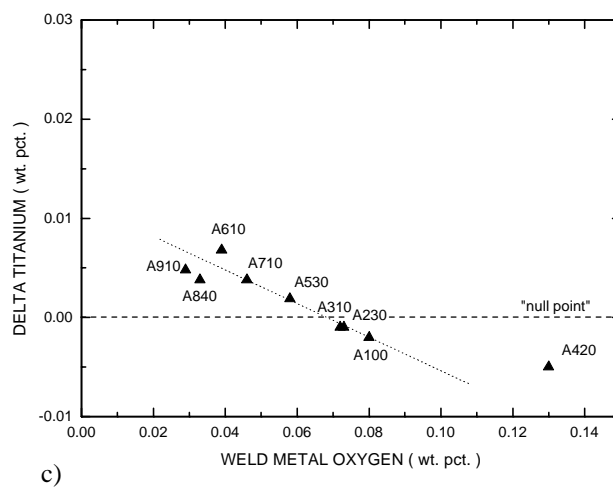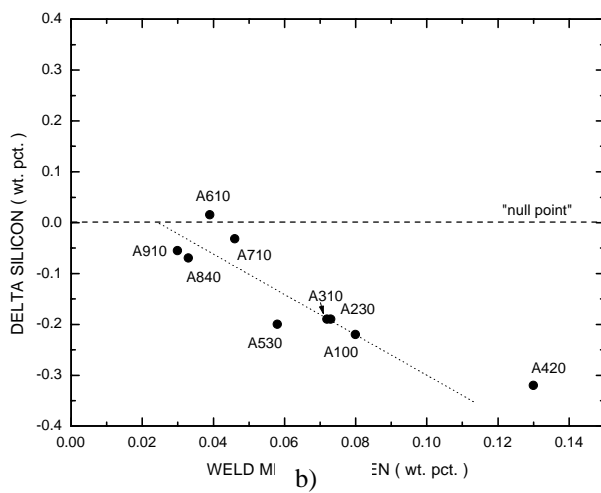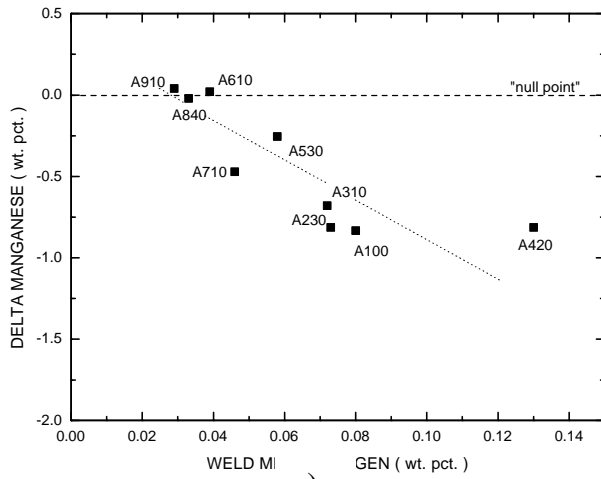

a)

b)

c)

Figure 4. Weld Metal Delta Quantity of: a) Manganese, b) Silicon, and
c) Titanium as a Function of Weld Metal Oxygen Content.

Table II. The Effect of Ferro-manganese Additions on Weld Metal Manganese
and Manganese Delta Quantity for the A5xx Electrodes.

Electrode Designation	Ferro-manganese Addition (wt.pct.)	Weld Metal Manganese Content (wt.pct.)	Manganese Delta Quantity (wt.pct.)
A420	2.2	0.26	-0.79
A510	4.2	0.39	-0.68
A520	6.2	0.64	-0.45
A530	8.2	0.83	-0.24

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 Figure 3, will directly result in the larger variations in alloy content.

Table III. The Effect of Ferro-titanium Additions on Weld Metal Titanium
and Titanium Delta Quantity for the A6xx Electrodes.

Electrode Designation	Ferro-titanium Addition (wt.pct.)	Weld Metal Titanium Content (wt.pct.)	Titanium Delta Quantity (wt.pct.)
A530	0.0	0.007	-0.002
A610	2.0	0.017	0.007
A620	4.0	0.021	0.011
A630	6.0	0.029	0.020
A640	9.0	0.036	0.027

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 5 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. pct. 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.
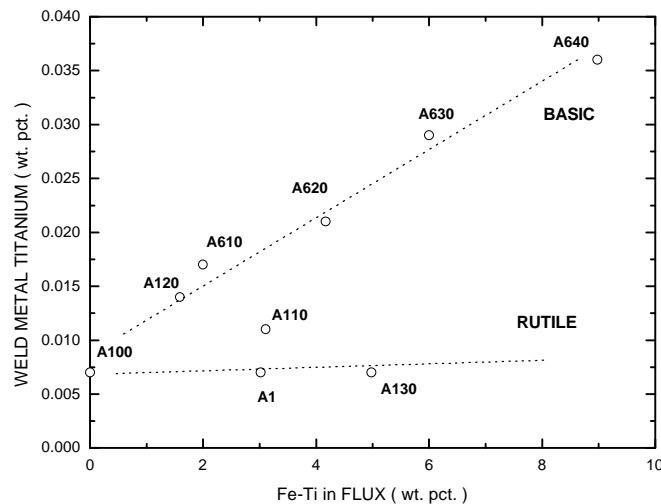

Figure 5. Weld Metal Titanium Content as a Function of Fe-Ti Additions in the Flux.

As illustrated in Figure 4.b, 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 multi-pass welding. Therefore, further optimization of the weld metal alloy content that takes into consideration the final weld metal properties and the multiple pass weld sequence, often required in structural fabrication, is essential to create a welding electrode that will deposit a suitable weld metal. 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.

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, Figure 6, which led to improved mechanical properties.
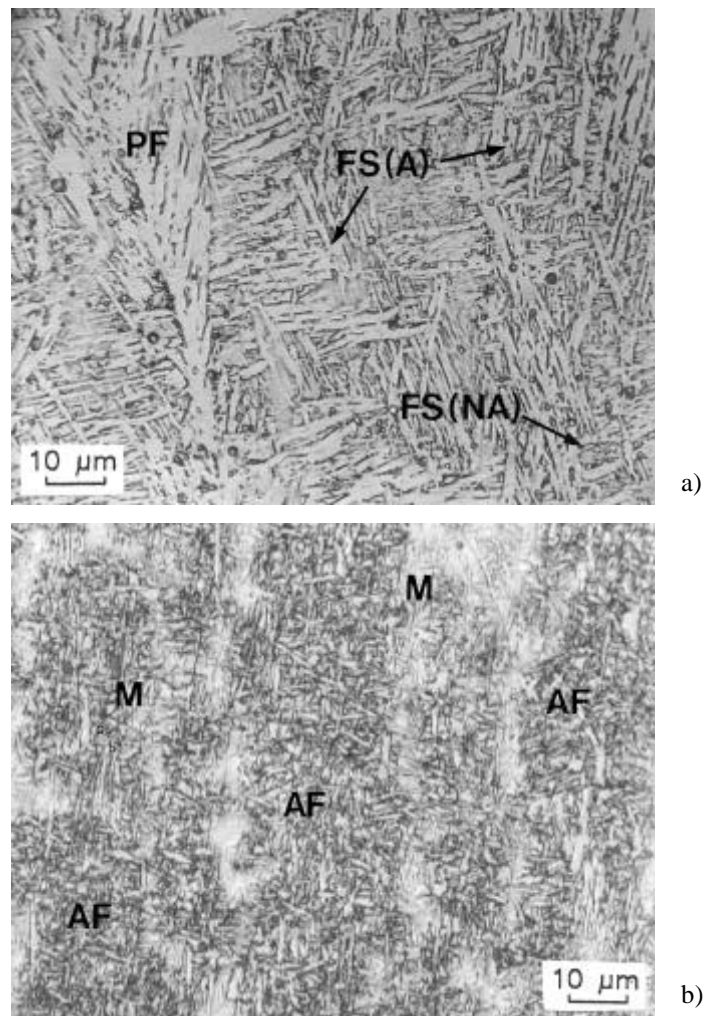

Figure 6. Weld Metal Microstructure as a Function of the Flux Composition. A) Rutile-base flux – A100, b) "Basic" flux – A630. PF - Primary Ferrite, FS(A) – Ferrite Sideplate Aligned, FS(NA) – Ferrite Sideplate Non-aligned, M – Martensite, AF – Acicular Ferrite.

CONCLUSIONS

The extensive SMA welding electrode-coating investigation conducted in this work has led to an understanding of the formulation 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 on the weld metal chemical composition.

2. A reference 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 sideplate ferrite and promoted the formation of acicular ferrite, bainite and martensite.

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

ACKNOWLEDGMENTS

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