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Reducing Diffusible Hydrogen Contents of Shielded Metal Arc Welds Through Addition of Flux-Oxidizing Ingredients

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This investigation examined the feasibility of using flux modification in the form of the addition of oxidizing ingredients to reduce the as-deposited hydrogen content of basic-type shielded metal arc welds. Additions of up to 16.3% micaceous iron oxide (MIO) to the flux formulation of an E7018-1 type electrode lowered the diffusible weld hydrogen content by approximately 70%. This can be attributed to the formation of oxygen, which lowers the partial pressure of hydrogen in the arc atmosphere, and the reaction of FeO (formed on dissociation of MIO) with hydrogen. The partitioning of deoxidizing elements (manganese and silicon) between the weld metal and slag on addition of MIO to the flux coating was also examined, but the influence of flux additions on the weld mechanical properties and the electrode operating characteristics was not evaluated during the course of this investigation.

Keywords hydrogen, flux, oxygen, shielded metal arc welding

1. Introduction

The prevention of hydrogen-induced cold cracking during the welding of ferritic steels, particularly higher-strength steels, remains a major concern despite extensive research into this phenomenon (Ref 1). A heavy responsibility is placed on the fabricator to incorporate appropriate safeguards against hydrogen-induced cracking in welding procedures. In addition to prescribing properly treated low-hydrogen basic-type welding consumables, fabricators rely on preheating, interpass temperature control, stringent heat input control, and postweld heat treatment to reduce the risk of cracking during welding. These traditional hydrogen control measures are costly and time-consuming.

During shielded metal arc welding (SMAW), the preheat and interpass temperatures required to prevent hydrogen-induced cracking are determined, in part, by the hydrogen potential of the welding consumable. An incentive therefore exists for welding consumable manufacturers to reduce the hydrogen content of basic-type SMAW electrodes by lowering baseline moisture contents and moisture pick-up rates. Current benchmarks are less than 3 mL hydrogen per 100 g of weld metal for SMAW electrodes, and less than 2 mL hydrogen per 100 g of weld metal for flux-cored arc welding (FCAW) consumables.

Published research suggests that the diffusible weld metal hydrogen content can be manipulated by arc chemistry modification through the use of flux additions (Ref 1-4). Most of these investigations, however, focused on submerged arc wire and flux systems and on flux-cored wires. These systems are simplistic in the sense that the flux formulations consist of a limited number of ingredients. Very little has been reported on hydrogen control through arc chemistry modification for the more complex flux systems of SMAW electrodes. A number of the hydrogen reduction strategies developed for SAW and FCAW systems, however, hold potential for reducing the diffusible hydrogen content of shielded metal arc welds through modification of the electrode coating formulation. Some of these hydrogen reduction strategies are briefly summarized below:

- Reducing the amount of hydrogen entering the weld pool by modifying the chemistry of the arc plasma through additions of oxidizing ingredients or fluoride-containing compounds to the flux formulation.
- Increasing the slag basicity in order to increase the slag water capacity and thereby prevent the dissolution of hydrogen into the weld pool.
- Decreasing the partial pressure of hydrogen in the arc to reduce the amount of hydrogen absorbed by the weld metal.
- Adding ingredients to the flux formulation that react with hydrogen to form insoluble hydrogen-containing products in the liquid iron.

The influence of the addition of various fluoride-containing compounds and changes in slag basicity through the addition of calcite to the flux formulation has been investigated and is described elsewhere (Ref 5). The emphasis of this report is on the effect of the addition of oxidizing ingredients to the electrode coating of basic-type SMAW electrodes on the diffusible weld metal hydrogen content.

The presence of oxidizing ingredients in the electrode coating is expected to influence the weld metal hydrogen content mainly through the introduction of oxygen into the arc atmosphere on decomposition. The influence of oxygen on hydrogen absorption during welding can be explained on the

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basis of the decomposition of moisture in the arc atmosphere, as represented by Eq 1. In this equation, H_2O is in the gaseous state, while $\underline{O}$ and $\underline{H}$ denote oxygen and hydrogen dissolved in the liquid steel.

$$H_2O\,(g) \leftrightarrow 2\underline{H} + \underline{O} \qquad \text{(Eq 1)}$$

According to Le Chatelier's principle, an increase in the oxygen content of the arc atmosphere during welding should encourage Eq 1 to proceed to the left. This removes atomic hydrogen from the arc atmosphere, effectively reducing the partial pressure of hydrogen in contact with the liquid weld metal. At the low hydrogen levels normally present in the arc atmosphere during SMAW with basic electrodes, Sieverts' law predicts a corresponding decrease in the absorbed hydrogen content of the weld metal. Increasing the oxygen level in the arc is therefore expected to lead to a reduction in the weld metal hydrogen content.

One potential drawback of this method is that the weld may contain higher-oxygen levels after welding, which may have a detrimental effect on the weld metal mechanical properties. High levels of oxygen in the weld metal can also result in excessive losses of deoxidizingelements (such as manganese and silicon) to the slag. Depletion of manganese and silicon from the weld metal may have a negative impact on mechanical properties.

It must be emphasized that this project examined the influence of flux chemistry on the diffusible hydrogen content of welds. The effect of variations in flux composition on the operating characteristics of the electrodes or the properties of the weld metal was not evaluated.

2. Experimental Procedure

2.1 Experimental Electrode Production

During the course of this investigation, a series of experimental electrodes with different flux formulations was produced in small batches (1 kg flux each) in the development laboratory at the Afrox Welding Consumable Factory in Brits, South Africa. The raw materials used to produce the flux mixtures were typical of the ingredients used in the normal day-to-day production of electrodes in the factory.

The coating composition of an E7018-1 basic-type welding electrode was selected as reference formulation. This flux formulation is normally very complex, containing up to 16 different ingredients, with the following major compounds (as approximate percentages):

- Fluorspar (CaF_2) 22%
- Calcite ($CaCO_3$) and dolomite ($CaCO_3.MgCO_3$) 20%
- Iron powder 31%
- Slag formers, binders, extrusion aids, and deoxidizers 27%

The dry raw materials were weighed and blended in a small-blade mixer for approximately 7 min to obtain a homogeneous mixture. Raw materials from the same batches were used throughout the investigation. A liquid silicate binder was then added to the dry flux mixture, followed by mixing for a further 10 min. The binder consisted of a complex mixture of various alkali silicates with a wide range of viscosities. The flux was then extruded onto a 4 mm diameter mild-steel core wire using a coating factor of 1.67, where the coating factor represents the ratio of the core wire diameter to the final electrode diameter. Core wire from the same cast was used for all the experimental electrodes.

After extrusion the electrodes were baked in accordance with the prescribed cycle for an E7018-1 type electrode. The baking cycle consisted of 2 h at 180 °C, followed by a further 2 h at 460 °C.

2.2 Experimental Flux Formulations

In order to evaluate the influence of oxidizing additions to the flux formulation on the diffusible weld metal hydrogen content, micaceous iron oxide (MIO) was added to the standard electrode flux formulation to increase the amount of oxygen available in the arc. MIO is a naturally occurring mineral ore, also known as specular hematite. The MIO used as raw material in this investigation contained a minimum of 90% Fe_2O_3 and a maximum of 4% SiO_2.

The MIO was first added to the standard flux formulation without varying any of the other ingredients. This resulted in progressive dilution of the other flux ingredients with increasing MIO content. The following flux formulations were produced:

- No MIO addition (the reference flux formulation),
- addition of 2.4% MIO,
- addition of 4.7% MIO,
- addition of 8.9% MIO, and
- addition of 16.3% MIO.

In a second series of experimental electrodes, the iron powder in the reference formulation was progressively substituted with MIO. The sum total of the weight percentages of MIO and iron powder in the coating therefore remained constant at about 31% (the reference flux iron powder content). The substitutions were done in the following way:

- No substitution (the reference electrode formulation),
- 2.4% MIO,
- 4.9% MIO,
- 9.8% MIO,
- 19.5% MIO, and
- 31.2% (total substitution of iron powder with MIO).

2.3 Determination of the Diffusible Weld Metal Hydrogen Content

The hydrogen content of each weld was determined using the standard laboratory method applied at the welding consumable factory. This method is based on the procedure described in ISO 3690: "Procedure for determining the hydrogen content in arc weld metal," but a Yanaco G-1006H gas chromatograph was used to measure the diffusible weld metal hydrogen, instead of the more traditional mercury method. An investigation by an American Welding Society task group indicated that the reproducibility and reliability of this test method is ±1 mL hydrogen per 100 g weld metal. Similar levels of reproducibility and reliability have been reported by an Australian study (Ref 6).

ISO 3690 specifies the sampling and analytical procedure for the determination of diffusible and residual hydrogen in ferritic weld metal. The test consists of a single weld bead deposited under controlled conditions. This weld is rapidly quenched after welding and stored at −78 °C or lower until analyzed. In order to ensure repeatability, the same welder was used to produce all the experimental welds in this investigation. The welding parameters were maintained at 185 A (15 A less than the maximum recommended by the manufacturer for the reference E7018-1 electrode) and 23 V.

After measuring the amount of weld metal hydrogen, the values were corrected for standard temperature, atmospheric pressure, and humidity conditions.

3. Results and Discussion

3.1 Diffusible Weld Metal Hydrogen Contents

The diffusible weld metal hydrogen contents measured for the experimental welds are shown in Fig. 1. Each data point shown in Fig. 1 refers to the average of eight hydrogen measurements, whereas the error bars represent the range from the minimum to the maximum hydrogen level measured in each formulation.

As shown in Fig. 1, the addition of MIO to the flux formulation resulted in a significant reduction in the diffusible weld metal hydrogen content. The presence of 16.3% MIO in the flux coating reduced the weld metal hydrogen content by almost 70%, compared to the hydrogen level measured in the reference formulation. The mechanism responsible for this reduction in weld metal hydrogen content can be explained by considering the chemical reactions that take place in the weld pool and the arc during welding.

The MIO decomposes in the arc during welding to form FeO. A portion of this FeO reacts with hydrogen, as illustrated by the reaction shown in Eq 2. This reduces the weld metal hydrogen content.

$$\mathrm{FeO} + 2\mathrm{H} \leftrightarrow \mathrm{Fe} + \mathrm{H_2O}\ (\mathrm{g}) \qquad \text{(Eq 2)}$$

At the same time, the partial pressure of hydrogen in the arc is reduced due to dilution of the arc atmosphere with oxygen liberated on dissociation of the H_2O formed as a product of reaction (2). This dissociation reaction is represented by Eq 1. According to Le Chatelier's principle, any increase in the dissolved oxygen content of the weld metal drives reaction (1) to the left, removing hydrogen from solution. The standard free energy, ΔG°, of the moisture dissociation reaction, Eq 1, is given by Eq 3, where T is the temperature (Ref 7).

$$\Delta G^\circ = 46.18 + 1.57\,T \qquad \text{(Eq 3)}$$

The equilibrium constant for Eq 1, K_1, is given by Eq 4, where $P_{\mathrm{H_2O}}$ is the partial pressure of H_2O in the welding arc.

$$K_1 = \frac{[\underline{\mathrm{H}}]^2[\underline{\mathrm{O}}]}{P_{\mathrm{H_2O}}} \qquad \text{(Eq 4)}$$

If the dissolved hydrogen content, $[\underline{\mathrm{H}}]$, is shown graphically as a function of the dissolved oxygen content, $[\underline{\mathrm{O}}]$, it is evident from Fig. 2 that an inverse relationship exists. As the dissolved oxygen content of the weld pool increases, the hydrogen content of the weld metal decreases. Figure 2, however, also suggests that, given a specific flux composition and oxygen content, the residual weld metal hydrogen content cannot be reduced below a specific threshold value (determined by the thermodynamics of the system).

It therefore appears likely that the observed reduction in weld metal hydrogen content with increasing levels of MIO in the flux cannot be attributed simply to an increase in the weld metal oxygen concentration. The formation of FeO on decomposition of MIO during welding is also expected to play a role. The formation of a monolayer of FeO at the slag/metal interface has been shown to prevent hydrogen adsorption from the arc atmosphere on welding with fluxes containing oxidizing ingredients (Ref 9). This is expected to reduce the amount of hydrogen that enters the weld pool from the arc during welding. The addition of MIO to the flux formulation also increases the flux basicity. The basicity index of flux is usually calculated by dividing the total weight percentage of basic flux components by the sum of the acidic and amphoteric components. The most widely used empirical basicity index equation was developed by Tuliani et al. (Ref 10), and is shown in Eq 5.

$$B = \frac{\mathrm{CaO+MgO+BaO+K_2O+Li_2O+CaF_2+0.5(MnO+FeO)}}{\mathrm{SiO_2+0.5(Al_2O_3+TiO_2+ZrO_2)}} \qquad \text{(Eq 5)}$$

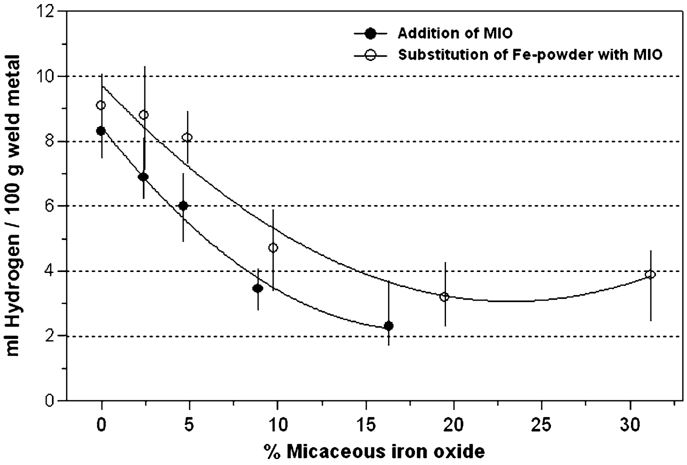

Fig. 1 Diffusible weld metal hydrogen contents measured as a function of MIO content for flux formulations containing an MIO addition, and for coatings where the iron powder in the reference formulation was progressively substituted with MIO

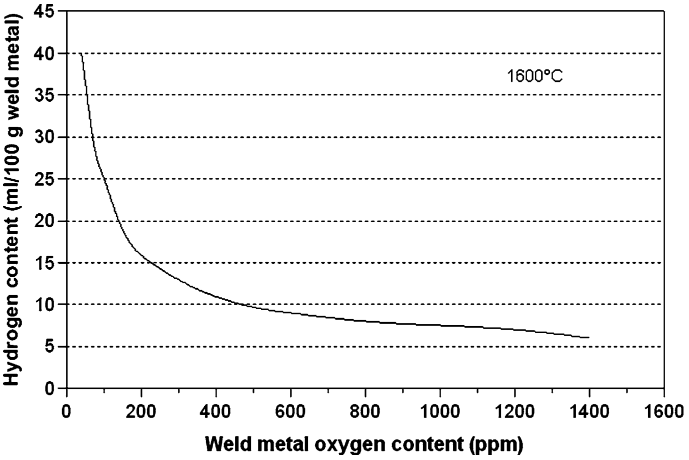

Fig. 2 The relationship between the dissolved weld metal oxygen and hydrogen contents (Ref 8)

Each basic or acidic ingredient in Eq 5 is represented by its weight percentage in the flux formulation. According to the International Institute of Welding, a flux is termed acidic when the basicity index is less than 1, neutral when it is between 1 and 1.5, semi-basic when it is between 1.5 and 2.5, and basic when the basicity index is greater than 2.5. Equation 5 indicates that the presence of FeO raises the flux basicity. A more basic flux has been shown to reduce the weld metal hydrogen content (Ref 11, 12).

As shown in Fig. 1, substitution of the iron powder in the reference flux formulation with up to 16.3% MIO also reduced the weld metal hydrogen content. Substitution of iron powder with MIO, however, has a less pronounced effect on the weld metal hydrogen level than addition of MIO, resulting in higher weld metal hydrogen contents for a given MIO content in the flux. This can be attributed to differences in the flux-oxidizing ingredient content, as well as to changes in the basicity of the system. Substitution of iron powder with more than 19.3% MIO did not decrease the weld metal hydrogen content significantly. Higher levels of MIO even appeared to cause a slight increase in the diffusible weld metal hydrogen content. This increase in weld metal hydrogen at higher levels of oxidizing ingredients in the flux has also been reported by De Medeiros and Liu (Ref 13) for SMAW electrodes designed for underwater wet welding.

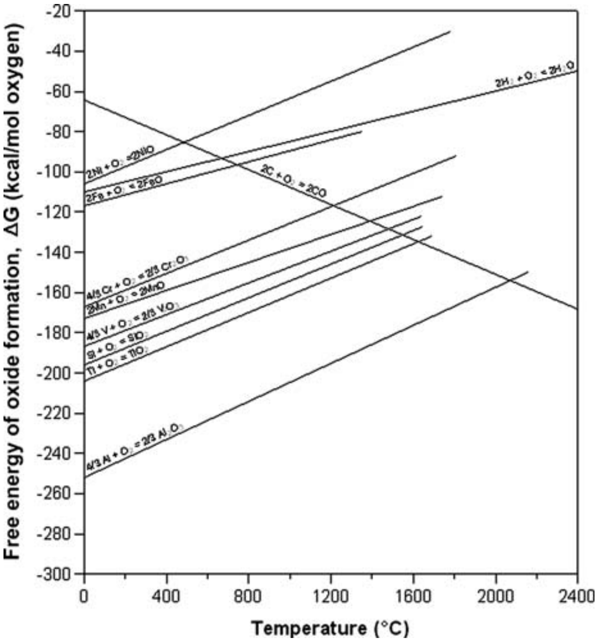

Fig. 3 Partial Richardson-Ellingham diagram (redrawn) (Ref 14)

3.2 Deoxidation in the Weld Pool

Although it has been shown that an increase in the level of oxidizing compounds in the flux formulation has a beneficial effect on the weld metal hydrogen content, such an increase is likely to influence the deoxidation reactions in the weld pool. An increase in oxygen content is expected to affect the partitioning of deoxidizers, particularly manganese and silicon, between the weld metal and the slag, and can potentially influence the mechanical properties of the weld metal. In order to examine the influence of MIO additions to the flux formulation on the partitioning of deoxidizing elements between the weld metal and the slag, the likely deoxidation reactions in the weld pool were examined.

Primary deoxidation of the weld pool occurs when oxide inclusions form in the weld pool and separate from the liquid metal to gather in the slag. The Richardson-Ellingham diagram (shown in Fig. 3) displays the free energy of formation of various oxides as a function of temperature, and suggests that silicon reacts with oxygen before manganese to deoxidize the weld pool.

Figure 4 compares the deoxidant (silicon and manganese) content of the weld metal with the amount of hydrogen on addition of MIO to the flux formulation. The weld metal silicon declined rapidly with increasing MIO content until almost no silicon remained in the weld metal at a MIO content of approximately 8.8%. With an increase in flux MIO content, the weld metal manganese content initially decreased slowly, but the rate increased slightly as silicon was consumed and manganese became the dominant deoxidant in the weld metal. Increasing the amount of oxidizers in the flux therefore resulted in a significant decrease in the concentration of deoxidizers in the weld metal. This can be attributed to the deoxidizing elements reacting with the excess oxygen introduced by the MIO in the flux, and being transferred to the slag.

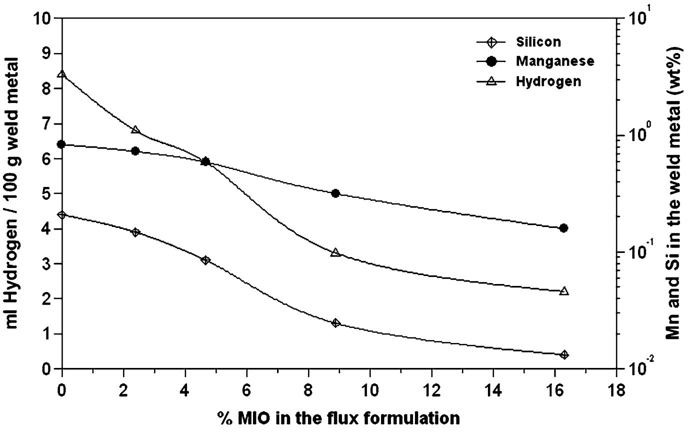

Fig. 4 The influence of MIO flux additions on the deoxidant concentration in the weld metal

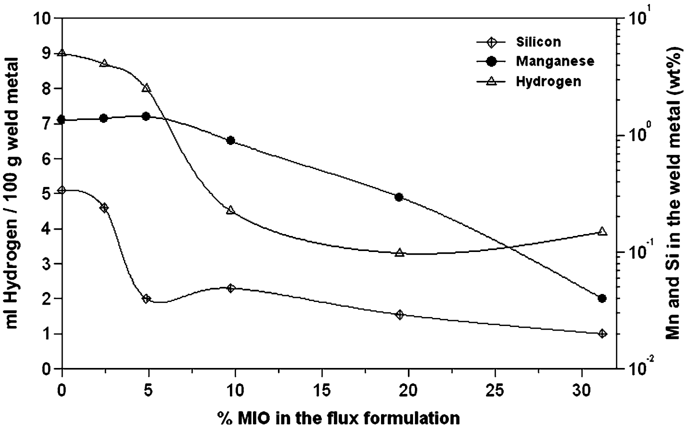

Fig. 5 The influence of the substitution of iron powder with MIO in the flux formulation on the deoxidation reactions in the weld metal

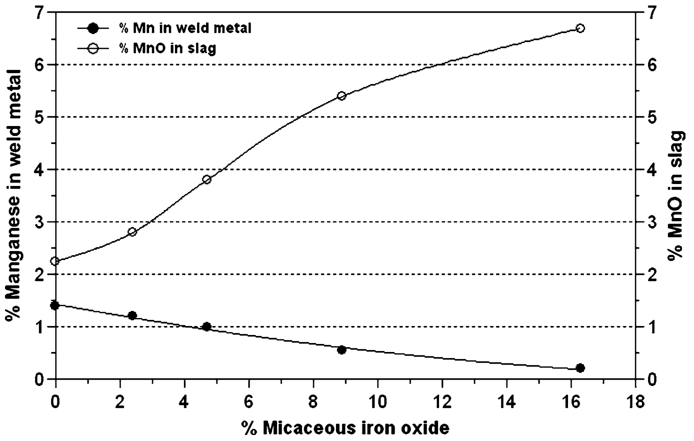

Fig. 6 Partitioning of manganese between the weld metal and slag with the addition of MIO to the flux formulation

Deoxidation in the weld pool on substitution of the flux iron powder by MIO resulted in a slightly different trend (Fig. 5). Initially the weld metal manganese content remained almost constant and a significant decrease in silicon content was observed. At flux MIO contents greater than about 4.8%, the weld metal manganese concentration started declining as manganese becomes dominant in the deoxidation sequence.

It can therefore be concluded that below a threshold concentration of oxidizing ingredients in the flux, deoxidation was primarily due to the reaction of oxygen with silicon. As the

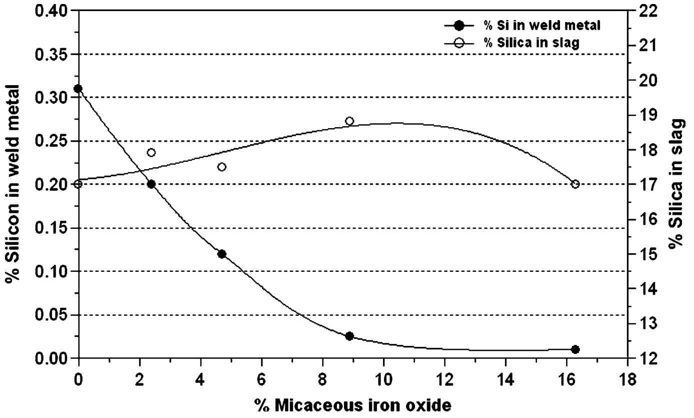

Fig. 7 Partitioning of silicon between the weld metal and slag with the addition of MIO to the flux formulation

flux oxidizing content increased, more silicon was consumed. Once most of the silicon had been consumed, manganese became the dominant deoxidizer in the pool. This is in agreement with the predictions of the Richardson-Ellingham diagram shown in Fig. 3.

An attempt was also made to examine the influence of MIO additions to the reference flux formulation on the partitioning of manganese and silicon between the weld metal and the slag during welding. This was done by analyzing the compositions of both the weld metal and the slag of the experimental welds.

As shown in Fig. 6, the amount of manganese in the weld metal decreased with increasing flux MIO content, whereas the amount of manganese oxide in the slag increased. This can be attributed to an increase in the oxygen content of the weld pool with an increase in flux MIO content. More manganese therefore took part in the deoxidation reaction shown in Eq 6. The MnO formed as product of this reaction partitioned to the slag, reducing the weld pool manganese content.

$$\underline{\mathrm{Mn}} + \underline{\mathrm{O}} = \mathrm{MnO}\ (\mathrm{slag}) \qquad \text{(Eq 6)}$$

A similar trend was observed for the partitioning of silicon, as shown in Fig. 7. The amount of silicon available for deoxidation in the weld pool was small compared to the amount of manganese in the experimental welds. The trend was therefore not as pronounced as that observed for manganese.

The addition of oxidizing ingredients to the flux therefore holds potential for the welding consumable manufacturer as a means of lowering the diffusible weld metal hydrogen content. However, one has to guard against raising the weld metal oxygen content too high as it may negatively affect the weld metal mechanical properties. Determining optimal levels of deoxidizing ingredients in the flux with respect to welding properties and weld metal mechanical properties did not form part of this investigation, and this aspect will therefore not be considered further here.

4. Conclusions

The prevalence of hydrogen-induced cracking during the welding of ferritic steels often necessitates the use of stringent welding procedures, including the use of low-hydrogen welding consumables, preheating and interpass temperature control, postweld heat treatment, and strict heat input control during welding. An incentive exists for welding consumable manufacturers to reduce the hydrogen potential of basic-type SMAW electrodes. During the course of this project, the influence of the addition of oxidizing ingredients to the electrode coating of an E7018-1 basic-type electrode on the diffusible weld metal hydrogen content was examined.

The addition of oxidizing ingredients to the reference flux formulation (in the form of MIO) lowered the diffusible weld metal hydrogen content. Reductions in weld metal hydrogen of almost 70% were achieved with the addition of up to 16.3% MIO. This can be attributed to the formation of oxygen, which lowers the partial pressure of hydrogen in the arc atmosphere, and the reaction of FeO (formed on dissociation of MIO) with hydrogen. The addition of MIO to the flux coating affected the partitioning of deoxidizing elements (manganese and silicon) between the weld metal and slag.

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