

Sources of Weld Metal Oxygen Contamination During Submerged Arc Welding

The oxygen level of submerged arc weld metal is controlled by SiO₂ decomposition in most acidic fluxes whereas the oxygen level of basic fluxes is controlled by the oxygen potential of the slag as determined by the FeO content of the slag.

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ABSTRACT. Thermodynamic calculations have been made for several possible rate controlling slag-metal reactions involving oxygen. The results, coupled with experimental data, suggest probable mechanisms of weld metal oxygen contamination and provide guidelines for design and selection of welding consumables. It is further shown that fluxes with basicities greater than those currently being produced should not provide significant reductions in weld metal oxygen content and may in fact be harmful.

Introduction

Ever increasing concern for the fracture toughness of weldments has led to recent investigations of weld metal oxygen content. These investigations have shown that oxygen content decreases as flux basicity increases.^{1,2} The explanation for this trend is by no means obvious when one considers that the oxygen potential of these fluxes is not a uniform function of flux basicity. In fact, for equivalent FeO contents, the oxygen potential reaches a maximum at the value of basicity index for which oxygen content is a minimum. Such a trend is surprising to say the least.

In an effort to understand the mechanism of weld metal oxygen contamination, thermodynamic calculations have been performed for several possible slag-metal reactions. The result of these calculations, coupled with available experimental data provides an explanation of the observed phenomena in terms of rate controlling slag-

metal reactions. In turn, the assumption that these reactions are controlling, makes it possible to formulate semi-quantitative rules for the selection of flux compositions and sheds further light on the overall mechanisms of weld metal oxygen contamination.

Previous Work

The literature on slag-metal reactions in welding is limited, with the majority of the studies having been performed on high FeO and high acid fluxes,^{3,4} both of which result in high weld metal oxygen content, with resultant low toughness. It has been recognized for over 15 years that high flux basicity will reduce oxygen levels and improve toughness.^{5,6} Recently, there has been an effort to achieve even higher flux basicities in hopes of further improving toughness.

Much of the experimental data reported in the literature is insufficient for meaningful thermodynamic calculations. The minimum data required involve:

1. Total flux chemistry before welding.

2. Total slag chemistry after welding.

3. Weld metal chemistry.

It is also useful or even necessary to have:

4. Welding electrode chemistry.
5. Base metal chemistry.
6. Percent dilution.
7. Ratio of slag weight to weight of weld metal deposited.
8. Operating conditions, viz., weld current, voltage, travel speed, cooling rate, etc.

Such data permit numerous calculations which aid in determining the controlling reactions during submerged arc welding.

No single source could be found which provided all of the above data; however, one paper, by Tuliani et al.,² was conspicuous in the abundance of data presented, and half of the experimental data used in this paper are taken from that work. Sufficient data on four other welds were found in a paper by Garland and Kirkwood.¹ Information on five additional welds is shown in Table 1, and was supplied from the files of a commercial firm.

The basicity index used in this paper is given by:

$$BI = [\text{CaO} + \text{MgO} + \text{BaO} + \text{SrO} +$$

$$\text{Na}_2\text{O} + \text{K}_2\text{O} + \text{Li}_2\text{O} +$$

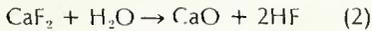
$$\frac{1}{2} (\text{MnO} + \text{FeO})] / [\text{SiO}_2 +$$

$$\frac{1}{2} (\text{Al}_2\text{O}_3 + \text{TiO}_2 + \text{ZrO}_2)] \quad (1)$$

Paper to be presented at the AWS 59th Annual Meeting in New Orleans during April 3-7, 1978.

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which is identical with the equation given by Tuliani *et al.*² and later used by others,⁷⁻⁹ except for the omission of CaF₂ as a basic component of the flux. Equation (1) represents the practice, common in steelmaking literature and verified by at least two separate studies,^{10,11} of assuming CaF₂ as a neutral component in slags. In welding, a trend toward a slight decrease in CaF₂ level after flux usage may be most likely attributed to the reaction:



This reaction is known to proceed rapidly,¹² and is a much more important source of fluorine loss than the reduction of CaF₂ by Si to form SiF₄, as has been suggested by others.² Equation (2) also represents an important reason for the use of dry welding fluxes, as HF formation poses a serious health hazard when fluoride fluxes are used.

The trend toward decreasing weld metal oxygen level with increasing basicity is not altered by the use of equation (1) rather than Tuliani's formula, but is shifted in value slightly as is shown in Fig. 1. The available data appear to fit either index equally well; however, it is felt that the basicity index represented by equation (1) is preferable as it is supported by thermodynamic measurements. If the activity of SiO₂ is not altered by addition of CaF₂ to steelmaking slags, there is no reason to presume that it should be altered in welding fluxes.

Sources of Weld Metal Oxygen

High toughness steel plates are either fully killed or at least semi-killed to maintain base metal oxygen levels below approximately 100 ppm. Many welding electrodes formulated for high toughness applications are vacuum melted for an oxygen content which is also below 100 ppm,⁹ yet the very lowest weld metal oxygen levels are approximately 200-300 ppm.

The excess oxygen content, above the base metal or electrode oxygen contents, must come from either one or both of two sources, i.e., the surrounding atmosphere or decomposition of oxide components in the flux. It is primarily this latter source with which this paper is concerned, although it is argued, later in the paper, that atmospheric contamination may be a significant factor, particularly in the more basic fluxes.

The general trend of the weld metal oxygen content as a function of flux basicity is shown in Fig. 1b. It is seen that the oxygen level decreases monotonically up to a basicity of 1.25 and is constant at approximately 250 ppm from thereon. As mentioned previous-

Table 1.—Weld Metal, Slag and Flux Chemistries for Five Submerged Arc Weldments A to E Using Commercial Fluxes

	^(a) Weld letter designation				
	A	B	C	D	E
<i>Weld Metal Chemistry</i>					
C	.19	.18	.22	.18	.19
Mn	1.21	.94	1.02	.80	1.06
Si	.25	.38	.20	.49	.12
O ^(b) (ppm)	270	544	208	536	201
<i>Flux/Slag Chemistry</i>					
SiO ₂	41.0/39.2	40.1/37.4	33.9/33.1	54.1/49.4	12.9/11.9
Al ₂ O ₃	1.3/1.4	6.1/6.3	4.9/5.3	4.8/4.3	18.1/18.2
TiO ₂	-/-	16.2/15.8	3.7/3.7	-/-	0.6/0.6
FeO	0.4/1.9	1.0/3.9	0.4/0.9	0.2/3.5	2.2/2.4
MnO	4.0/4.5	11.5/12.2	0.3/1.3	0.3/2.0	0.3/1.2
CaO	46.2/44.7	18.9/18.2	46.8/46.2	27.5/27.6	10.2/8.1
CaF ₂	-/-	4.5/4.3	6.6/6.4	3.9/3.7	26.7/26.8
MgO	1.0/1.8	1.4/1.4	2.0/1.7	9.6/9.6	28.2/28.4
Total	93.9/93.5	99.7/99.5	98.6/98.6	100.4/100.1	99.2/97.6
Bl—eq (1)	1.18/-	0.52/-	1.29/-	0.66/-	1.78/-
Bl—Tuliani <i>et al.</i> ²	1.18/-	0.6/-	1.4/-	0.7/-	3.01/-

^(a)Base metal and electrode compositions are not available but were uniform for each weld. Welding was single pass using DCEP.

^(b)Oxygen analysis determined by neutron activation.

ly, this trend contradicts the trend which would be expected when one considers only the oxygen potential of the flux, which is determined by the activity of FeO in the flux.

It is seen in Fig. 2, that the FeO activity has a pronounced peak at a basicity = 2, which corresponds to the orthosilicate composition in the SiO₂—CaO system.

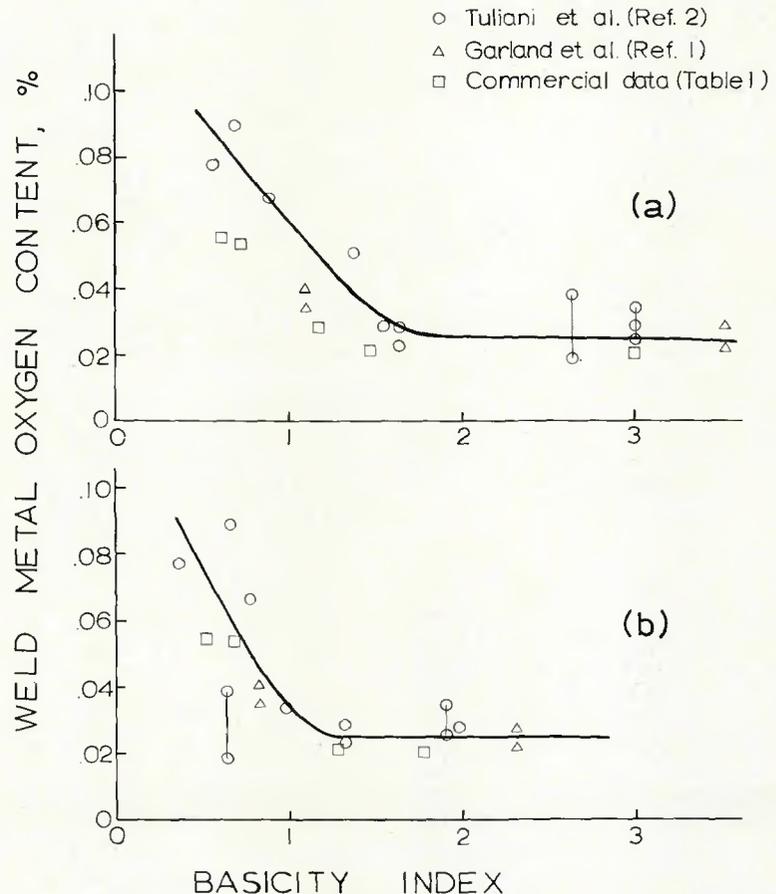


Fig. 1—Weld metal oxygen content as a function of flux basicity. The top curve is graphed using Tuliani's equation for flux basicity which includes CaF₂ as a basic component in the flux. The bottom graph represents the same experimental data plotted against a basicity index which treats CaF₂ as a neutral component—eq (1)

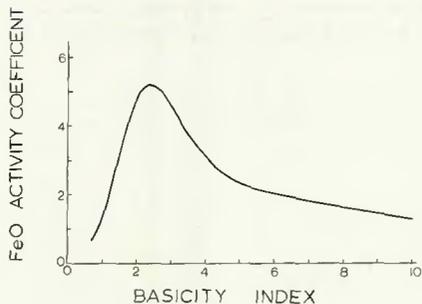
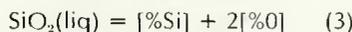


Fig. 2—The activity coefficient of a dilute solution of FeO in oxide fluxes as a function of basicity—plotted from data taken from McGannon¹³

A comparison of Figs. 1 and 2 and Table 1 shows that the oxygen content of weld metal is not a simple function of the oxygen potential of the flux, even when variations in slag FeO content are taken into account. This conclusion leads to a consideration of other possible slag-metal reactions which might control weld metal oxygen content.

The SiO₂ Reaction

Belton et al.⁴ have shown that, for a wide variety of acid fluxes, the weld metal silicon content can be represented by the following reaction:



$$\log_{10} K = \frac{-28,360}{T} + 10.61,$$

$$K = \frac{[\% \text{Si}][\% \text{O}]^2}{\% \text{SiO}_2}$$

if a reaction temperature of 2000 C (3632 F) is chosen for equilibrium.

If the FeO content is less than 10%, this relationship also provides a measure of the weld metal oxygen content. It should be noted that the effective reaction temperature of 2000 C (3632 F) is in agreement with other measurements of the weld pool temperature.¹⁴

It appears that for acid slags, at least, reaction (3) may be considered to approach equilibrium during welding. Using this assumption, the oxygen content of weld metal in equilibrium with SiO₂ - CaO slags at 2000 C (3632 F) of varying basicity is plotted in Fig. 3. A family of curves is generated to account for the initial silicon content of the weld metal. Clearly the higher activity of SiO₂ in the more acidic fluxes may explain the high dissolved oxygen contents found in welds made under these fluxes. Reaction (3) does not, however, explain the relatively constant weld metal oxygen level for the basic fluxes. In order to explain this

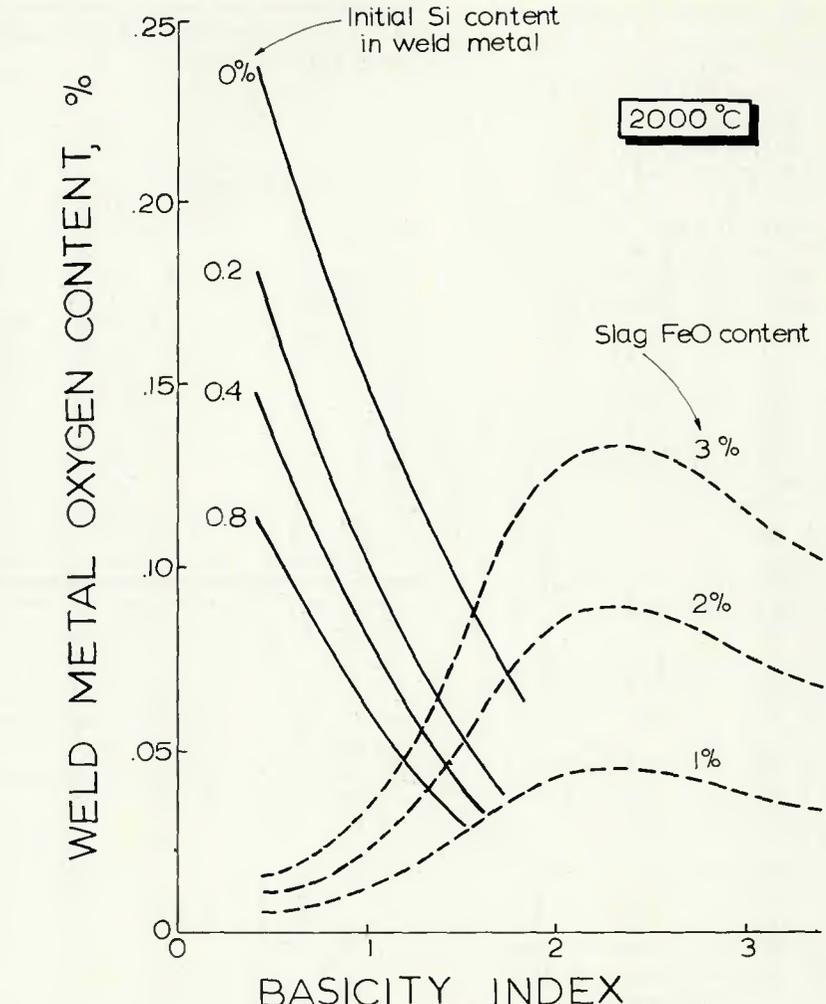


Fig. 3—Dissolved oxygen equilibrium at 2000 C as a function of basicity index in SiO₂ - CaO and SiO₂-CaO-FeO slags over Fe-Si melts. SiO₂ equilibrium data from Belton, et al.,⁴ FeO equilibrium data from McGannon¹³

trend it is necessary to consider other reactions which control oxygen content under these fluxes.

The FeO Reaction

Figure 3 also shows the weld metal oxygen equilibrium at 2000 C (3632 F) to be expected from the following reaction:



$$\log K = \frac{6372}{T} - 2.73$$

The peak in FeO activity at BI \approx 2, shown in Fig. 2, is evident, as well as a tendency for relatively low levels of FeO to provide oxygen to the weld metal no matter how large the basicity index.

It is not suggested that the FeO reaction achieves equilibrium at 2000 C (3632 F) during welding; in fact, the experimental data indicate that this reaction does not reach equilibrium.⁴ It is important to note, however, that

Fig. 3 illustrates the direction in which the FeO reaction is expected to proceed. For slags with a basicity greater than 1.25 and greater than 1% FeO, the FeO reaction should proceed from right to left and would be expected to be a source of weld metal oxygen. For basicities less than 1.25, a reaction represented by the sum of the SiO₂ and FeO reactions is expected, with the dissolution of SiO₂ in the weld pool representing a fast step and the absorption of FeO by the flux representing a slower step.

Combining the above reactions provides a reasonable explanation for the variation of weld metal oxygen as shown in Fig. 1. The assumptions used are:

1. That the effective reaction temperature in the weld pool is 2000 C (3632 F).
2. That the SiO₂ reaction is fast and proceeds to completion.
3. That the FeO reaction provides an upper limit on the expected oxygen levels for the more basic fluxes, but does not achieve equilibrium.

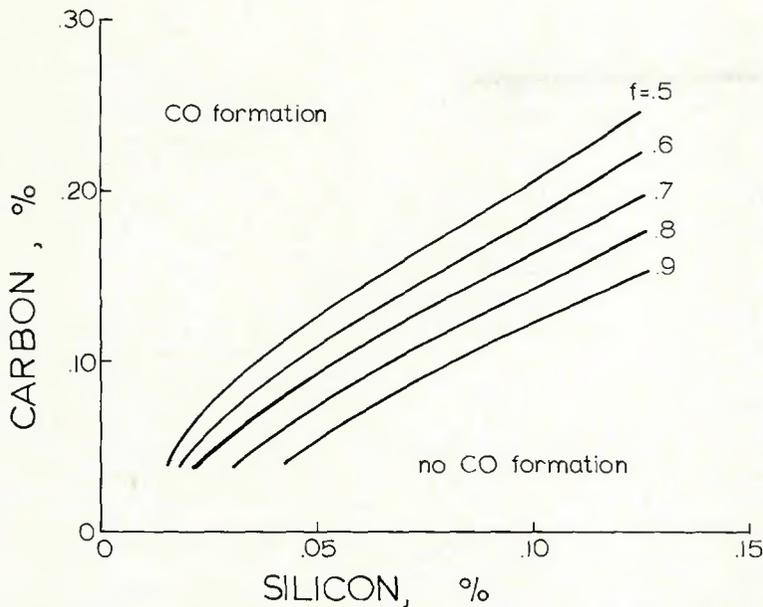
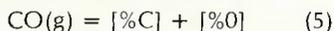


Fig. 4—The weld metal silicon content required to suppress CO gas formation (one atmosphere) as a function of weld metal carbon content for various fractions solid—after Wright and Elliott¹⁵

Using the above assumptions we find that the weld metal oxygen level is controlled by the SiO₂ activity in acid fluxes (BI < 1.25) and is a strong function of basicity. The oxygen level is controlled by the FeO activity in the more basic fluxes, where the activity of SiO₂ becomes negligible, and is effectively independent of basicity. These assumptions and conclusions are confirmed by the experimental data.

The CO Reaction

If we consider the reaction:



$$\log K = \frac{-1168}{T} - 2.07$$

we find that for weld metal carbon levels around 0.10%C, the CO reaction would predict oxygen levels somewhat below those actually observed.

Such an equilibrium would result in reduction of weld metal carbon level and evolution of CO gas with resultant porosity in the weld metal. However, Wright and Elliott¹⁵ have shown that Si is effective in suppressing formation of CO gas—Fig. 4. Thus CO porosity is not a problem in most weld metals, where the Si content is above 0.10%. It should be noted, however, that highly basic fluxes do reduce the weld metal silicon levels to very low values which may permit CO gas evolution. For this reason, care should be taken when welding low carbon steels with highly basic fluxes, i.e., basicity greater than 2.

The MnO Reaction

Christensen has found that the

following reaction



$$\log K = \frac{-12,810}{T} - 5.65$$

does not proceed to completion.^{3,16} Indeed, the experimental data indicate that the MnO reaction is the most sluggish of all the reactions yet considered. It is only possible, therefore, to predict the direction in which the reaction will proceed for a given flux-weld metal combination.

If we assume a weld metal oxygen level as shown in Fig. 1b, we may calculate the equilibrium MnO content of the slag for a given [%Mn] in the weld metal as a function of basicity, as is shown in Fig. 5. If the %MnO in the flux is less than the equilibrium value, reaction (6) will proceed from left to right and will have a deoxidizing effect upon the weld metal. If the initial MnO concentration in the flux is greater than the equilibrium value, MnO will be dissolved in the weld metal and will become a source of oxygen, and the assumption that the SiO₂ and FeO reactions alone are controlling weld metal oxygen content becomes invalid.

Fortunately, for all but one of the data available, the MnO reaction proceeds from left to right and contributes to deoxidation of the weld metal. This fact is in reasonable agreement with the predictions of Fig. 5.

An important conclusion that may be reached from Fig. 5 is that the MnO content should be reduced as far as practical in basic fluxes, while MnO may be tolerated in significant

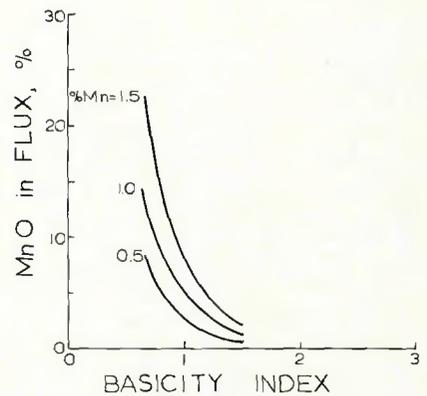


Fig. 5—The equilibrium concentration of MnO at 2000 C in MnO-SiO₂-CaO slags as a function of basicity index assuming 0.5, 1.0 and 1.5% Mn in the metal pool and an oxygen concentration as shown in Fig. 1 (b). Activities of MnO at 2000 C estimated from the data in McGannon¹⁸

amounts in more acidic fluxes.

The Oxygen Balance

An oxygen balance may be applied on our flux-weld metal-slag system such that SiO₂ dissolved in the weld metal produces oxygen which may be found as either weld metal oxygen or increased MnO and FeO in the slag. If this occurs, we find an excess of oxygen in the final weld metal-slag system when compared with the starting weld metal-flux system.

In this analysis we assume that SiO₂, FeO and MnO are the only reactive components in the flux (a reasonable assumption since virtually no Al, Ca, Mg, Ti, Na, or K is found in the final weld metal). The balance is difficult to determine accurately since no specific data are available from weldments where percent dilution, weld metal-to-slag weight ratio and electrode, flux, base metal, slag and weld metal chemistries, are given. However, using the electrode, flux, base plate, slag and weld metal chemistries of Tuliani et al⁹ and estimating that anywhere from 1/3 to 1/2 pound of flux is consumed per pound of weld metal⁸ and assuming 50% dilution in the weld, we find that oxygen is generally in great excess, particularly in the more basic fluxes.

The conclusion is that oxygen must be entering the weldment from the surrounding atmosphere, and that this contamination is probably more severe under basic fluxes. Qualitatively, this atmospheric contamination might be expected to be more severe when welding under the basic fluxes since these fluxes are generally more fluid than high SiO₂ fluxes.¹³ This increased fluidity may allow the slag cover to flow away from the molten weld pool under the forces of the arc plasma jet. The jet in turn causes entrainment of air within the arc cavity which results

in higher weld metal oxygen and slag FeO levels than would otherwise be expected.

It is interesting to note that in the alternate process of electroslag welding using fluxes free of SiO₂, both highly basic and highly acidic, the weld metal oxygen levels are never greater than 100 ppm.⁷ Such levels are characteristic of Si-Mn deoxidation practice and suggest that the FeO content of the slag must be low, even though the same slag is molten for a much longer period of time than is characteristic of submerged arc welding.

Again, such data suggest that the higher oxygen levels experienced in submerged arc welding may not be explained solely in terms of the relevant slag-metal reactions. An external source of oxygen contamination should be considered as a significant factor in submerged arc welding.

Discussion

The general form of the weld metal oxygen level vs. flux composition curve does not follow the oxygen potential of the flux directly, due to the rapid dissolution of SiO₂ in acidic fluxes. It thus may be possible to formulate acidic fluxes which are low in SiO₂¹⁷ and which could achieve low weld metal oxygen levels with resulting increases in toughness. Such fluxes would most probably be based on TiO₂ and/or Al₂O₃.

As has been suggested by Palm,¹⁸ and as is shown in Fig. 3, higher base metal Si levels inhibit the dissolution of SiO₂ and aid in reducing weld metal oxygen content in acidic fluxes. Specifications for base metal Si levels are currently limited to approximately 0.5% Si maximum, because Si has a reputation for lowering weld metal toughness. These specifications should be re-examined to determine the true effect of Si on weld metal toughness. If the Si in the weld metal comes from decomposed SiO₂, then high Si weld metals would not be expected to be tough, due to concurrent oxygen contamination. However, if the weld metal Si content is derived from the base plate and welding electrode, it would not be nearly as harmful to toughness, and in some cases may be beneficial.¹⁸⁻²⁰

Previous results, using acidic fluxes only, which showed a correlation of Si weld metal content with decreased toughness, may in fact not have recognized the possibly more important correlation of oxygen content with toughness in these weldments. Certainly the acceptable Si content of the base metal is important, in that the carbon equivalent must be maintained below an acceptable level to prevent

cracking. However, with current trends toward lower carbon steels, Si levels might be effectively increased without either reducing toughness or exceeding acceptable carbon equivalents.

Many current specifications do not allow this freedom in alloy design. A limited number of experiments have been performed which confirm the conclusion that higher Si in the base metal does not harm metal toughness.²⁰

Conclusion

In conclusion, the suggested model for oxygen contamination of submerged arc weld metal implies the following:

1. The oxygen level of submerged arc weld metal is controlled by SiO₂ decomposition in most low FeO acidic fluxes; 2000 C (3632 F) represents an effective equilibrium temperature.

2. The oxygen level of basic fluxes is controlled by the oxygen potential of the slag which is determined by the FeO content of the slag; the reaction cannot be represented by a single effective equilibrium reaction temperature.

3. Basic slags may exhibit excessive FeO and MnO contents due to atmospheric contamination caused by increased slag fluidity.

4. The flux basicity index is only an indirect measure of the oxygen level of the weld metal. The correlation should more properly be drawn between oxygen level and SiO₂ and/or FeO activity in the slag.

5. It is preferable to treat CaF₂ as a neutral component when calculating flux basicity.

6. The MnO and FeO content of the flux become more critical the higher the flux basicity.

7. More complete data are needed in order to determine which slag metal reactions are controlling weld metal oxygen level.

8. Welding process variables such as current voltage, travel speed and cooling rate have a potential effect on weld metal oxygen level through control of atmospheric contamination and time of reaction.

9. Higher Si levels in the base plate or electrode may be effective in improving weld metal toughness under certain conditions, and

10. When welding very low carbon steels with high basicity fluxes, high silicon welding electrodes should be used to suppress CO gas formation.

Acknowledgment

The author wishes to express his appreciation to Professor T.B. King for several helpful discussions concerning this work.

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