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Evaluation of Flux Basicity Concept Geared toward Estimation for Oxygen Content in Submerged Arc Welded Metal

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Abstract: The present study has been undertaken to evaluate the basicity concept of oxygen content estimation subject to submerged arc welded metal. The investigated fluxes cover a wide range of basicity indices from 0.31 to 19.00 at full coverage with acidic, neutral, and basic fluxes. The oxygen content of the submerged arc welded metal (flux oxygen potential) is predicted by employing traditional flux basicity index models and the CALPHAD technique (gas–slag–metal equilibrium model). It is revealed that the gas–slag–metal equilibrium model in this study is capable of remedying the shortcomings of the basicity index models with respect to predicting the oxygen potentials of the fluxes with CaF₂, CaO, SiO₂, MnO, and FeO as major components. This study may provide a vital way to address technical difficulties in flux design. Based on the measured and thermodynamic data, thermodynamic parameters pertinent to flux oxygen potential have been systematically assessed.

Keywords: weld metal; CALPHAD technique; flux design; basicity; composition control; composition prediction

1. Introduction

Submerged arc welding (SAW), during which the arc plasma and weld pool are shielded beneath the flux granular and molten slag, is one of the most widely applied welding techniques [1]. Flux serves essential functions in the SAW process, including atmospheric protection, arc stabilization, fine-tuning weld metal (WM) composition, etc. [2]. Due to chemical reactions between arc plasma, flux(slag), and weld pool, the flux essentially affects the composition of the submerged arc welded metal [3–5].

O is the most essential element dictating WM mechanical properties [6,7]. Excessive oxygen levels may incur unexpected issues, such as enhanced porosity, reduced toughness, and depreciated hardenability, whereas WM with oxygen levels that are too low shows poor impact toughness, since there are insufficient inclusions to promote the formation of acicular ferrite [8,9]. Additionally, the oxygen content in the WM essentially controls the transfer behaviors of alloying elements, which dictates the mechanical properties of the weldment [6,7]. Therefore, the content of the oxygen content in SAW is of great importance to ensure the quality of the overall submerged arc welded metal.

In the presence of the plasma during the SAW process, oxides in flux tend to decompose, release O₂, and improve the oxygen level in the weld pool [10,11]. It is well known that welding flux is the primary source of oxygen transfer to the WM [7,12]. In welding metallurgy, the concept of flux oxygen potential has been employed to describe the driving force for oxygen transfer from the flux (slag) to the WM [3,13–15].

Due to the incomplete understanding of flux thermodynamic properties, the prediction of oxygen levels in submerged arc welded metal relied on empirical ideas drawn from
Some basic oxides, such as FeO and MnO, possess high oxygen potentials, whereas CaO does not, indicating that CaF does not, indicating that

\[
BI = \frac{CaO + CaF + MgO + Na_2O + K_2O + 0.5 \times (MnO + FeO)}{SiO_2 + 1/2(Al_2O_3 + Cr_2O_3 + TiO_2 + ZrO_2)}
\]  

The oxygen-free compound contained in flux is CaF. The basic oxides include CaO, CaF, MgO, Na_2O, K_2O, MnO, and FeO, and the acid oxides include SiO_2, Al_2O_3, Cr_2O_3, TiO_2, and ZrO_2.

Eagar [6], on the other hand, assumed that CaF only acts as a dilutant rather than an active species, and declared that CaF should be removed from Equation (1). Then, the Eagar BI is proposed as Equation (2) [6]. Based on the value BI, fluxes can be classified into three categories: acidic (BI < 1.0), neutral (1 \leq BI < 1.2), and basic (BI \geq 1.2) [13].

\[
BI = \frac{CaO + MgO + Na_2O + K_2O + 0.5 \times (MnO + FeO)}{SiO_2 + 1/2(Al_2O_3 + Cr_2O_3 + TiO_2 + ZrO_2)}
\]  

Tuliani et al. [17] and Eagar [6] have regressed the tendencies of the WM oxygen level (oxygen content in the submerged arc welded metal) as a function of flux BI, as shown in Figure 1, from which the WM oxygen could be predicted. Generally, the predicted oxygen content decreases with increasing BI and then reaches a constant.

However, Palm et al. [18] pointed out that there is no fundamental basis for the correlation between BI and flux oxygen potential. For example:

1. Some basic oxides, such as FeO and MnO, possess high oxygen potentials, whereas CaO does not, indicating that BI may identify flux oxygen potential inaccurately.
2. When BI is higher than 2.2, the predicted oxygen content will hold constant. In other words, the BI models would be invalid in differentiating flux oxygen potential when BI is higher than 2.5 (see the blue shaded area in Figure 1).
3. It is still questionable whether CaF should be incorporated into the BI formula.

![Figure 1](image-url)
Tremendous efforts have been exercised to investigate the parameter governing the flux oxygen potential. For instance, Lau et al. [7,12] evaluated the source of oxygen when CaO-Al2O3-based fluxes were applied; they postulated that the level of \( p_{O_2} \) (partial pressure of \( O_2 \) in the arc plasma) deriving from oxide decomposition controlled the level of flux oxygen potential. Indacochea et al. [19] performed SAW by using FeO-MnO-SiO2 fluxes and analyzed the chemical reactions. They assumed that the level of flux oxygen potential is a function of the equilibrium FeO activity at the slag–metal interface.

It is noted that there are several issues complicating the investigation of flux O potential, subject to SAW [5,20,21].
1. Since the arc plasma, molten slag, and weld pool are shielded under the flux granular, it is impossible to capture the gases in the arc plasma or to sample the molten slag for analytical purposes.
2. The temperature of chemical reactions in SAW is as high as 2000 °C, at which the thermodynamic data remain scarce.

Hopefully, a number of thermodynamic databases for gases, oxides, and alloy systems have been developed via the CALPHAD technique in recent decades [22–26]. Although the temperature of SAW is much higher than the traditional metallurgy process, the thermodynamic databases could be extended to higher temperatures by using the applicable thermodynamic models, such as the cell model, the modified regular solution model, etc. [23]

It is widely accepted that equilibrium is not attained due to the high temperature and large density gradients in the SAW process [2,19,27]. Despite this, we could assume that the state of thermodynamic equilibrium is attained locally, on the basis that the high temperatures and high surface-to-volume ratio counteract the short time available for reactions to be completed. As such, one may place constraints on the chemical reactions and element transfer behaviors between different phases [19,27–29].

Recently, Sengupta et al. [1] have summarized the physical phenomena in SAW. Then, based on the work of Sengupta et al. [1], Zhang et al. [9] concluded the existing state of the plasma(gas)–slag–gas interface (see Figure 2), and performed the gas–slag–metal equilibrium calculation to analyze the formations of the gases [3].

![Figure 2. Schematic diagram of SAW and gas-associated reaction interface.](image)

The objective of the present study has been to evaluate the concept of flux basicity geared toward flux oxygen potential estimation. Typical fluxes of five systems are poised to be employed within this framework, including FeO-SiO2-MnO, CaO-SiO2-MnO, CaFe2SiO2-MnO, CaF2-SiO2, and CaF2-MnO fluxes. This covers a wide range of flux BIs from
0.31 to 19.00, including acidic, neutral, and basic fluxes. Then, the gas–slag–metal equilibrium model is proposed, the capabilities of models to predict flux oxygen potential are systemically assessed, and the factor governing the prediction accuracy for flux oxygen potential is evaluated. Additionally, thermodynamic parameters pertinent to flux oxygen potential are systemically assessed. This study is concerned essentially with CaF$_2$, CaO, SiO$_2$, MnO, and FeO, since they are the most common components for flux design.

2. Materials and Methods

Table 1 summarizes the fluxes to be discussed in this work. The processes of flux preparations, welding experiments, and compositional analysis processes are given in the literature in the ‘Data source’ column of Table 1.

The LECO analyzer was used to determine the contents of oxygen. The WM oxygen content is predicted from $Bl$ (see Table 1) by using curves in Figure 1.

The Equilib module of FactSage (version 7.3, CRCT, Montreal, Canada and GTT, Aachen, Germany) was employed to establish the gas–slag–metal equilibrium model, as follows [3–5,21,30]:

1. FToxid, Fstel, and FactPS databases were selected. Solution phases of ASlag-liq all oxides, S (FToxid-SLAGA), and LIQUID (FStel-Liqu) were selected to model the molten slag and steel phases.
2. The equilibrium temperature in SAW of 2000 °C was set.
3. Nominal compositions, which refer to the contents considering only the dilution effects of the BM and electrode, were used as the input metal chemistries. Nominal compositions are referenced from the data source given in Table 1.

Table 1. Summary of flux formulas in this study.

| Flux  | CaF$_2$ | CaO | SiO$_2$ | MnO | FeO | Tuliani $Bl$ | Eagar $Bl$ | Flux Developers and Data Source |
|-------|---------|-----|---------|-----|-----|-------------|-------------|---------------------------------|
| F-1-1 | 0       | 0   | 40      | 0   | 60  | 0.75        | 0.75        |                                 |
| F-1-2 | 0       | 0   | 40      | 10  | 50  | 0.75        | 0.75        |                                 |
| F-1-3 | 0       | 0   | 40      | 20  | 40  | 0.75        | 0.75        | Indacochea et al. [31]          |
| F-1-4 | 0       | 0   | 40      | 30  | 30  | 0.75        | 0.75        |                                 |
| F-1-5 | 0       | 0   | 40      | 40  | 20  | 0.75        | 0.75        |                                 |
| F-1-6 | 0       | 0   | 40      | 50  | 10  | 0.75        | 0.75        |                                 |
| F-2-1 | 0       | 35  | 40      | 25  | 0   | 0.938       | 0.938       |                                 |
| F-2-2 | 0       | 30  | 40      | 30  | 0   | 1.125       | 1.125       |                                 |
| F-2-3 | 0       | 25  | 40      | 35  | 0   | 1.063       | 1.063       |                                 |
| F-2-4 | 0       | 10  | 40      | 50  | 0   | 0.875       | 0.875       |                                 |
| F-2-5 | 0       | 5   | 40      | 55  | 0   | 0.813       | 0.813       |                                 |
| F-3-1 | 35      | 0   | 40      | 25  | 0   | 1.188       | 0.313       |                                 |
| F-3-2 | 30      | 0   | 40      | 30  | 0   | 1.125       | 0.375       |                                 |
| F-3-3 | 25      | 0   | 40      | 35  | 0   | 1.063       | 0.438       |                                 |
| F-3-4 | 15      | 0   | 40      | 45  | 0   | 0.938       | 0.563       |                                 |
| F-3-5 | 10      | 0   | 40      | 50  | 0   | 0.875       | 0.625       |                                 |
| F-3-6 | 5       | 0   | 40      | 55  | 0   | 0.813       | 0.688       |                                 |
| F-4-1 | 95      | 0   | 5       | 0   | 0   | 19.0        | -           |                                 |
| F-4-2 | 90      | 0   | 10      | 0   | 0   | 9.0         | -           |                                 |
| F-4-3 | 80      | 0   | 20      | 0   | 0   | 4.0         | -           |                                 |
| F-4-4 | 70      | 0   | 30      | 0   | 0   | 2.3         | -           |                                 |
| F-5-1 | 95      | 0   | 0       | 5   | 0   | -           | -           |                                 |
| F-5-2 | 85      | 0   | 0       | 15  | 0   | -           | -           |                                 |
| F-5-3 | 78      | 0   | 0       | 22  | 0   | -           | -           |                                 |
| F-5-4 | 70      | 0   | 0       | 30  | 0   | -           | -           |                                 |
3. Results and Discussion
3.1. Acidic Flux with Low BI (BI = 0.75)

FeO-SiO$_2$-MnO fluxes are typical manganese-silicate fluxes with low BIs. It is well known that the O potential of FeO is higher than that of MnO [10]. However, such a difference cannot be identified by the BI models.

According to Equations (1) and (2), varying the relative amounts of MnO and FeO will not change the BI, nor will it change the predicted oxygen level. For instance, when the SiO$_2$ content is held constant at 40 wt pct, both Tuliani and Eagar BIs are at 0.75 (see Table 1).

The measured oxygen content and predicted value from BI models are shown in Figure 3. It is seen that, with a higher addition level of FeO (MnO is substituted by FeO), the oxygen content in the WM increases from 930 to 1410 ppm. The oxygen content predicted from the Tuliani BI model holds constant at 560 ppm, while that predicted from the Eagar BI model holds constant at 400 ppm. Both Tuliani and Eagar BI models fail to differentiate the oxygen potential of FeO and MnO.

![Figure 3. WM oxygen content as a function FeO content in flux.](image)

The oxygen content predicted from the gas–slag–metal equilibrium model is plotted in Figure 4. It is seen that the gas–slag–metal equilibrium model can correctly predict the increasing trend of oxygen content with FeO level. The inner chart of Figure 4 plotted the predicted equilibrium $p_{O_2}$ as a function of FeO level in flux, from which increasing equilibrium $p_{O_2}$ with FeO content is observed. Such information is in agreement with the assumption proposed by Lau et al. [7]. Therefore, the prediction accuracy has been improved via the application of the gas–slag–metal equilibrium model, since the impact of $O_2$ on the flux oxygen potential is considered.
3.2. Flux with Moderate BI (0.3 < BI < 1.2)

CaO-SiO$_2$-MnO and CaF$_2$-SiO$_2$-MnO fluxes were developed from FeO-SiO$_2$-MnO fluxes. For these fluxes, FeO is substituted by the components with lower oxygen potential (CaO or CaF$_2$). The selected CaO-SiO$_2$-MnO and CaF$_2$-SiO$_2$-MnO fluxes cover acidic, neutral, and basic fluxes with BI s spanning from 0.3 to 1.2.

As for CaO-SiO$_2$-MnO fluxes, the O content predicted using Tuliani and Eagar BI models is illustrated in Figure 5. It is widely accepted that the O potential of MnO is higher than that of CaO [10,34]. Therefore, with a higher level of MnO addition into flux (CaO is substituted by MnO), the measured O content improves from 610 to 950 ppm. Such a changing trend is predictable from both Tuliani and Eagar BI models, since the gain coefficient of CaO for BI is higher than that of MnO, as shown by Equations (1) and (2).

The content oxygen of the WM processed by CaF$_2$-SiO$_2$-MnO flux is plotted in Figure 6. Since CaF$_2$ is a component with no oxygen element, the substitution of CaF$_2$ with MnO would inevitably improve the flux oxygen potential. However, the reduction effect of CaF$_2$ on flux oxygen potential is not considered in the Eagar BI model; therefore, the Eagar BI decreases from 0.69 to 0.31 when MnO content increases from 25 to 55 wt pct, and lower predicted oxygen content from the Eagar BI model is anticipated. As shown in Figure 6, the changing trend in WM oxygen content with an MnO addition level is predictable using the Tuliani BI model, but it is incorrectly estimated by the Eagar BI model.
The content oxygen of the WM processed by CaF$_2$-SiO$_2$-MnO flux is plotted in Figure 6. Since CaF$_2$ is a component with no oxygen element, the substitution of CaF$_2$ with MnO would inevitably improve the flux oxygen potential. However, the reduction effect of CaF$_2$ on flux oxygen potential is not considered in the Eagar BI model; therefore, the Eagar BI decreases from 0.69 to 0.31 when MnO content increases from 25 to 55 wt pct, and lower predicted oxygen content from the Eagar BI model is anticipated. As shown in Figure 6, the changing trend in WM oxygen content with an MnO addition level is predictable using the Tuliani BI model, but it is incorrectly estimated by the Eagar BI model.

Another technical challenge is to differentiate the flux oxygen potential when CaF$_2$ is replaced by CaO, since CaO tends to change the activity of other oxides and complicates the chemical reaction subject to the SAW system. To address such technical difficulties, one may apply the gas–slag–metal equilibrium model by assuming the state of thermodynamic equilibrium is attained locally. The predicted oxygen content is plotted in Figure 7b. It is seen from Figure 7 that, for flux of the same MnO level, the substitution of CaF$_2$ by CaO initiates the improvement in flux oxygen potential (see the black and green shaded area in Figure 7a). Such improvements in flux oxygen potential can be predicted using the gas–slag–metal equilibrium model, as shown in Figure 7b. The inner chart indicates that the substitution of CaF$_2$ by CaO improves the level of equilibrium $p_{O2}$, which, in turn, promotes the flux oxygen potential level.
Another technical challenge is to differentiate the flux oxygen potential when CaF$_2$ is replaced by CaO, since CaO tends to change the activity of other oxides and complicates the chemical reaction subject to the SAW system [33]. To address such technical difficulties, one may apply the gas–slag–metal equilibrium model by assuming the state of thermodynamic equilibrium is attained locally. The predicted oxygen content is plotted in Figure 7b. It is seen from Figure 7 that, for flux of the same MnO level, the substitution of CaF$_2$ by CaO initiates the improvement in flux oxygen potential (see the black and green shaded area in Figure 7a). Such improvements in flux oxygen potential can be predicted using the gas–slag–metal equilibrium model, as shown in Figure 7b. The inner chart indicates that the substitution of CaF$_2$ by CaO improves the level of equilibrium $p_{O_2}$, which, in turn, promotes the flux oxygen potential level.

Figure 7. WM O content and equilibrium $p_{O_2}$ as a function of MnO content in flux.

3.3. Flux with High BI ($BI > 2.3$)

As mentioned previously, the BI models fail to differentiate the oxygen potential of fluxes when BI is higher than 2.2, since the predicted oxygen content would hold constant if BI is higher than 2.5, as shown in Figure 1.

As for CaF$_2$-SiO$_2$ fluxes, the Eagar BI holds constant at zero, since CaF$_2$ is excluded from the Eagar BI model, making the WM oxygen content unpredictable. The blue dots in Figure 8 show the predicted WM oxygen content from the Tuliani BI model. It is seen that the oxygen content predicted from the Tuliani BI model holds constant at 250 ppm. When the gas–slag–metal equilibrium model is applied, the increasingly changing trend of oxygen content with SiO$_2$ addition level is correctly predicted, as shown by the red triangles and black dots in Figure 8. The inner graph in Figure 8 illustrates that equilibrium $p_{O_2}$ increases from 8.26 to $17.9 \times 10^{-10}$ atm.

CaF$_2$-MnO fluxes are special basic ones, since only basic oxides are incorporated, making both Tuliani and Eagar BIs unpredictable, although MnO is the component possessing very high oxygen potential [10,34]. Nonetheless, the role of MnO in oxygen potential control can be reflected by the gas–slag–metal equilibrium model. It is seen from Figure 9 and its inner graph that both measured oxygen content and the one predicted from the gas–slag–metal equilibrium model increase with higher MnO content.
CaF$_2$-SiO$_2$

**Figure 8.** WM O content and equilibrium $pO_2$ as a function of SiO$_2$ content in flux.

Eagar BI Model: unapplicable!

**Figure 9.** WM O content and equilibrium $pO_2$ as a function MnO content in flux.
It is well known that MnO in flux tends to decompose into $O_2$ and significantly improves the oxygen level in the weld pool via Reaction (3). However, such a mechanism cannot be reflected in BI models. The gas–slag–metal equilibrium model, on the other hand, has taken the generation of $O_2$ into account. As shown by the inner graph in Figure 9, an improvement in equilibrium $p_{O_2}$ is observed with a higher level of MnO addition, since Reaction (3) is driven to the right side.

$$(\text{MnO}) = \text{Mn}(g) + \frac{1}{2}O_2(g) \quad (3)$$

When fluxes are designed, a common problem that people encounter is correctly differentiating the oxygen potential of $SiO_2$ and MnO, since they are the most frequently used components, yet have high oxygen potential [11]. The measured and predicted oxygen levels in Figure 10 illustrate that the oxygen potential of $SiO_2$ and MnO can be correctly distinguished when CaF$_2$-bearing fluxes are utilized.

![Figure 10. WM O content as a function of oxide content in flux.](image)

3.4. Bias between Equilibrium and Measured Oxygen Content

The measured and predicted oxygen data are summarized in Figure 11. It is seen from Figure 11 that only one dot falls into the red region, illustrating that the equilibrium oxygen content is higher than the measured one. This could be explained by the assumption discussed above; that is, the overall equilibrium could not be attained in SAW, which may provide experimental evidence for the assumption, subject to the non-thermodynamic-equilibrium status in the SAW process.

As was reported in the work of Zhang and Coetsee et al. [34], although thermodynamic equilibrium is not attained in the SAW process, the status of chemical reactions is closer to equilibrium under higher heat input. The typical kinetic model has been developed by Mitra et al. [35] However, to the knowledge of the authors, there are some deficiencies with respect to this model. We are investigating the transfer behavior that occurs when CaF$_2$-$SiO_2$-$Na_2O$ fluxes are applied under different heat inputs to evaluate the kinetic factors, which will be reported in our coming study.
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3.5. Role of CaF$_2$ in the Determination of Flux O Potential

The measured and predicted oxygen content indicates that the Eagar BI model may incorrectly predict the changing trend of flux oxygen potential, especially for CaF$_2$-enriched fluxes, since the deduction effect CaF$_2$ of flux oxygen potential is not considered in the Eagar BI model. For CaF$_2$-oxide binary fluxes, the Eagar BI model will be invalid, since the Eagar BI is incalculable.

Eagar [6] assumed that CaF$_2$ only acts as a dilutant rather than an active species. As such, he excluded CaF$_2$ from the Eagar BI model. However, as was reported by Coetsee et al. [3] and Zhang et al. [5], the chemical interaction between CaF$_2$ and oxides should be considered, as shown by Reaction (4).

$$2(CaF_2) + (MO_x) = 2(CaO) + MF_{2x}(g)$$

It is well known that CaO is the flux oxide component with the lowest oxygen potential [10]. Therefore, the oxides in flux are converted to CaO via Reaction (4), leading to a reduction in flux oxygen potential. This can be reflected by the significant reduction in CaF$_2$ levels and oxides after welding [36,37]. Gibbs free energy, surmised by Coetsee et al. [4], also confirms the occurrence of Reaction (4) in the SAW process. Hence, the consideration of CaF$_2$ as a dilutant rather than an active species may underestimate the overall flux oxygen potential.

4. Conclusions

This study has evaluated the flux basicity concept geared toward flux oxygen potential estimation in SAW. The flux oxygen potential (WM oxygen content) is predicted by using the Tuliani BI model, the Eagar BI model, and the gas–slag–metal equilibrium model. It is revealed that the gas–slag–metal equilibrium model is capable of remedying shortcomings of the BI models on differentiating oxygen potentials of the fluxes with CaF$_2$, CaO, SiO$_2$, MnO, and FeO as major components. The main findings can be summarized as follows:
1. For CaF$_2$-free fluxes, both Tuliani and Eagar $BI$ models fail to differentiate the oxygen potential of FeO and MnO. For CaF$_2$-enriched fluxes, the Eagar $BI$ model may incorrectly predict the changing trend of WM oxygen content as a function of the flux formula. Additionally, both Tuliani and Eagar $BI$ models fail to differentiate the oxygen potential of SiO$_2$ and MnO in CaF$_2$-based binary fluxes;

2. The gas–slag–metal equilibrium model can differentiate the oxygen potential of CaO, FeO, MnO, and SiO$_2$. Additionally, the gas–slag–metal equilibrium model is capable of estimating the changing trend of WM oxygen content, even when $BI$ models are inapplicable.

3. In comparison to flux $BI$, the gas–slag–metal equilibrium oxygen and $p_{O_2}$ is more feasible in differentiating the oxygen potential for fluxes of different formulas.

4. The measured data confirm that the overall equilibrium could not be attained in SAW, which may provide experimental evidence for assumptions subject to the non-thermodynamic-equilibrium status in SAW processes.

5. The sole consideration of CaF$_2$ being a dilutant rather than an active species may underestimate the flux oxygen potential.

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