



Guoyou Shao^{1,2}, Zhongqiu Liu², Jun Fan¹, Yan Guo¹, Qiong Xu¹ and Jin Zhang^{1,2,*}

- ¹ School of Mechanical and Electrical Engineering, Suqian University, Suqian 223800, China
- ² School of Metallurgy, Northeastern University, Shenyang 110819, China
- * Correspondence: 18142@squ.edu.cn

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



Citation: Shao, G.; Liu, Z.; Fan, J.; Guo, Y.; Xu, Q.; Zhang, J. Evaluation of Flux Basicity Concept Geared toward Estimation for Oxygen Content in Submerged Arc Welded Metal. *Metals* **2022**, *12*, 1530. https:// doi.org/10.3390/met12091530

Academic Editor: Michael Rethmeier

Received: 12 August 2022 Accepted: 13 September 2022 Published: 16 September 2022

Publisher's Note: MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.



Copyright: © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/).

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 O_2 , 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 steelmaking [2,16]. Tuliani et al. [17] have proposed a basicity index (*BI*), namely Tuliani *BI*, as is demonstrated in Equation (1) (wt pct), to identify flux oxygen potential.

$$BI = \frac{\text{CaO} + \text{CaF}_2 + \text{MgO} + \text{Na}_2\text{O} + \text{K}_2\text{O} + 0.5 \times (\text{MnO} + \text{FeO})}{\text{SiO}_2 + 1/2(\text{Al}_2\text{O}_3 + \text{Cr}_2\text{O}_3 + \text{TiO}_2 + \text{ZrO}_2)}$$
(1)

The oxygen-free compound contained in flux is CaF₂. The basic oxides include CaO, CaF₂, MgO, Na₂O, K₂O, MnO, and FeO, and the acid oxides include SiO₂, Al₂O₃, Cr₂O₃, TiO₂, and ZrO₂.

Eagar [6], on the other hand, assumed that CaF₂ only acts as a dilutant rather than an active species, and declared that CaF₂ 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 ($1 \le BI < 1.2$), and basic (*BI* ≥ 1.2) [13].

$$BI = \frac{\text{CaO} + \text{MgO} + \text{Na}_2\text{O} + \text{K}_2\text{O} + 0.5 \times (\text{MnO} + \text{FeO})}{\text{SiO}_2 + 1/2(\text{Al}_2\text{O}_3 + \text{Cr}_2\text{O}_3 + \text{TiO}_2 + \text{ZrO}_2)}$$
(2)

Tuliania 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.



Figure 1. Predicted WM O level as a function of flux *BI*.

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 CaF₂ should be incorporated into the *BI* formula.

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_{O2} (partial pressure of O₂ 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].

- 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.

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, CaF₂-SiO₂-MnO, CaF₂-SiO₂, and CaF₂-MnO fluxes. This covers a wide range of flux *BI*s 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 systematically assessed. This study is concerned essentially with CaF₂, CaO, SiO₂, 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 precited from *BI* (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]:

- 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.

| Flux | CaF ₂ | CaO | SiO ₂ | MnO | FeO | Tuliani BI | Eagar BI | Flux Developers and Data Source |
|-------|------------------|-----|------------------|-----|-----|------------|----------|---|
| F-1-1 | 0 | 0 | 40 | 0 | 60 | 0.75 | 0.75 | FeO-SiO ₂ -MnO Indacochea et al. [31] |
| F-1-2 | 0 | 0 | 40 | 10 | 50 | 0.75 | 0.75 | |
| F-1-3 | 0 | 0 | 40 | 20 | 40 | 0.75 | 0.75 | |
| 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 | CaO-SiO ₂ -MnO Burck et al. [32] |
| 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 | CaF ₂ -SiO ₂ -MnO |
| F-3-4 | 15 | 0 | 40 | 45 | 0 | 0.938 | 0.563 | Burck et al. [32] |
| 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 | - | CaF ₂ -SiO ₂ |
| F-4-3 | 80 | 0 | 20 | 0 | 0 | 4.0 | - | Dallam et al. [33] |
| 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 | - | - | CaF ₂ -MnO |
| F-5-3 | 78 | 0 | 0 | 22 | 0 | - | - | Chai et al. [10] |
| F-5-4 | 70 | 0 | 0 | 30 | 0 | - | - | |

Table 1. Summary of flux formulas in this study.

3.1. Acidic Flux with Low BI (BI = 0.75)

FeO-SiO₂-MnO fluxes are typical manganese-silicate fluxes with low *BI*s. 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 SiO₂ 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.

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_{O2} as a function of FeO level in flux, from which increasing equilibrium p_{O2} 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.



Figure 4. WM O content and equilibrium p_{O2} as a function FeO content in flux.

3.2. Flux with Moderate BI (0.3 < BI < 1.2)

CaO-SiO₂-MnO and CaF₂-SiO₂-MnO fluxes were developed from FeO-SiO₂-MnO fluxes. For these fluxes, FeO is substituted by the components with lower oxygen potential (CaO or CaF₂). The selected CaO-SiO₂-MnO and CaF₂-SiO₂-MnO fluxes cover acidic, neutral, and basic fluxes with *BI*s spanning from 0.3 to 1.2.

As for CaO-SiO₂-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 -SiO₂-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 precited 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.



Figure 5. WM O content as a function MnO content in flux.



Figure 6. WM O content as a function MnO content in flux.

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_{O2} , which, in turn, promotes the flux oxygen potential level.



Figure 7. WM O content and equilibrium p_{O2} 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 CaF₂-SiO₂ fluxes, the Eagar *BI* holds constant at zero, since CaF₂ 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 SiO₂ 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_{O2} increases from 8.26 to 17.9×10^{-10} atm.

CaF₂-MnO fluxes are special basic ones, since only basic oxides are incorporated, making both Tuliani and Eager *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.



Figure 8. WM O content and equilibrium p_{O2} as a function of SiO₂ content in flux.



Figure 9. WM O content and equilibrium p_{O2} 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_{O2} is observed with a higher level of MnO addition, since Reaction (3) is driven to the right side.

$$(MnO) = Mn(g) + \frac{1}{2}O_2(g)$$
 (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.

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 CaF₂-SiO₂-Na₂O fluxes are applied under different heat inputs to evaluate the kinetic factors, which will be reported in our coming study.



Figure 11. WM oxygen content as a function of oxide content in flux.

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 CaF₂-enriched fluxes, since the deduction effect CaF₂ of flux oxygen potential is not considered in the Eagar BI model. For CaF₂-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).

$$2(CaF_{2}) + (MO_{x}) = 2(CaO) + MF_{2x}(g)$$
(4)

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 CaF₂ 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 CaF₂ 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 CaF₂, CaO, SiO₂, MnO, and FeO as major components. The main findings can be summarized as follows:

- 1. For CaF₂-free fluxes, both Tuliani and Eagar *BI* models fail to differentiate the oxygen potential of FeO and MnO. For CaF₂-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 SiO₂ and MnO in CaF₂-based binary fluxes;
- 2. The gas–slag–metal equilibrium model can differentiate the oxygen potential of CaO, FeO, MnO, and SiO₂. 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_{O2} 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 CaF₂ being a dilutant rather than an active species may underestimate the flux oxygen potential.

Author Contributions: Conceptualization, G.S. and Z.L.; methodology, Y.G.; software, J.F.; validation, Q.X.; writing—review and editing, J.Z. All authors have read and agreed to the published version of the manuscript.

Funding: This work was financially supported by the National Natural Science Foundation of China (No. 52171031), the Fundamental Research Funds for the Central Universities (No. N2225011), the Opening project fund of Materials Service Safety Assessment Facilities (No. MSAF-2021-009), the Initial Fund of Suqian University (No. 2022XRC040), Suqian Sci&Tech Program (No. K202113), and Natural Science Research Program of Jiangsu Higher Education Institutions (No. 21KJB430015).

Conflicts of Interest: The authors declare no conflict of interest.

References

- Sengupta, V.; Havrylov, D.; Mendez, P. Physical Phenomena in the Weld Zone of Submerged Arc Welding-A Review. Weld. J. 2019, 98, 283–313. [CrossRef]
- Natalie, C.A.; Olson, D.L.; Blander, M. Physical and Chemical Behavior of Welding Fluxes. Annu. Rev. Mater. Sci. 1986, 16, 389–413. [CrossRef]
- Coetsee, T.; Mostert, R.J.; Pistorius, P.G.H.; Pistorius, P.C. The Effect of Flux Chemistry on Element Transfer in Submerged Arc Welding: Application of Thermochemical Modelling. J. Mater. Res. Technol. 2021, 11, 2021–2036. [CrossRef]
- Coetsee, T. Phase Chemistry of Submerged Arc Welding (SAW) Fluoride Based Slags. J. Mater. Res. Technol. 2020, 9, 9766–9776. [CrossRef]
- Zhang, J.; Coetsee, T.; Basu, S.; Wang, C. Impact of Gas Formation on the Transfer of Ti and O from TiO₂-bearing Basic-fluoride Fluxes to Submerged Arc Welded Metals: A Thermodynamic Approach. *Calphad* 2020, *71*, 102195. [CrossRef]
- 6. Eagar, T. Sources of Weld Metal Oxygen Contamination during Submerged Arc Welding. Weld. J. 1978, 57, 76–80.
- Lau, T.; Weatherly, G.; McLean, A. The Sources of Oxygen and Nitrogen Contamination in Submerged Arc Welding Using CaO-Al₂O₃ Based Fluxes. *Weld. J.* 1985, *64*, 343–347.
- Zhang, J.; Leng, J.; Wang, C. Tuning Weld Metal Mechanical Responses via Welding Flux Optimization of TiO₂ Content: Application into EH36 Shipbuilding Steel. *Metall. Mater. Trans. B* 2019, *50*, 2083–2087. [CrossRef]
- 9. Zhang, J.; Coetsee, T.; Dong, H.; Wang, C. Elucidating the Roles of SiO₂ and MnO upon Decarburization during Submerged Arc Welding: A Thermodynamic Study into EH36 Shipbuilding Steel. *Metall. Mater. Trans. B* **2020**, *51*, 1805–1812. [CrossRef]
- 10. Chai, C.; Eagar, T. Slag Metal Reactions in Binary CaF₂-Metal Oxide Welding Fluxes. Weld. J. 1982, 61, 229–232.
- 11. Kou, S. Welding Metallurgy, 3rd ed.; JohnWiley & Sons, Inc.: Hoboken, NJ, USA, 2003; pp. 22–122.
- Lau, T.; Weatherly, G.; McLean, A. Gas/metal/slag Reactions in Submerged Arc Welding Using CaO-Al₂O₃ Based Fluxes. *Weld. J.* 1986, 65, 31–38.
- Olson, D.; Liu, S.; Frost, R.; Edwards, G.; Fleming, D. Nature and Behavior of Fluxes Used for Welding. ASM Int. ASM Handb. 1993, 6, 55–63. [CrossRef]
- 14. Lao, Y.; Gao, Y.; Deng, F.; Wang, Q.; Li, G. Effects of Basicity and CaF₂ on the Viscosity of CaF₂-CaO-SiO₂ Slag for Electroslag Remelting Process. *Metall. Res. Technol.* **2019**, *116*, 638. [CrossRef]
- 15. Jindal, S.; Chhibber, R.; Mehta, N. Effect of Flux Constituents and Basicity Index on Mechanical Properties and Microstructural Evolution of Submerged Arc Welded high Strength Low Alloy Steel. *Mater. Sci. Forum* **2013**, 738–739, 242–246. [CrossRef]

- Liby, A.; Dixon, R.; Olson, D. Welding: Theory and Practice; Elsevier Science Publishers: Amsterdam, The Netherlands, 1990; pp. 151–169.
- 17. Tuliani, S.; Boniszewski, T.; Eaton, N. Notch Toughness of Commercial Submerged Arc Weld metal. *Weld. Met. Fabr.* **1969**, *37*, 327–339.
- 18. Palm, J. How Fluxes Determine the Metallurgical Properties of Submerged Arc Welds. Weld. J. 1972, 51, 358.
- Indacochea, J.E.; Blander, M.; Christensen, N.; Olson, D.L. Chemical Reactions During Submerged Arc Welding with FeO-MnO-SiO₂ Fluxes. *Metall. Trans. B* 1985, 16, 237–245. [CrossRef]
- Zhang, Y.; Zhang, J.; Liu, H.; Wang, Z.; Wang, C. Addressing Weld Metal Compositional Variations in EH36 Shipbuilding Steel Processed by CaF₂-SiO₂-CaO-TiO₂ Fluxes. *Metall. Mater. Trans. B* 2022, *53*, 1329–1334. [CrossRef]
- 21. Zhang, J.; Wang, C.; Coetsee, T. Thermodynamic Evaluation of Element Transfer Behaviors for Fused CaO-SiO₂-MnO Fluxes Subjected to High Heat Input Submerged Arc Welding. *Metall. Mater. Trans. B* **2021**, *52*, 1937–1944. [CrossRef]
- Bale, C.W.; Bélisle, E.; Chartrand, P.; Decterov, S.; Eriksson, G.; Gheribi, A.; Hack, K.; Jung, I.-H.; Kang, Y.-B.; Melançon, J. Reprint of: FactSage Thermochemical Software and Databases, 2010–2016. *Calphad* 2016, *55*, 1–19. [CrossRef]
- Jung, I.-H. Overview of the applications of thermodynamic databases to steelmaking processes. *Calphad* 2010, 34, 332–362. [CrossRef]
- Park, J.H. Solidification structure of CaO-SiO₂-MgO-Al₂O₃(-CaF₂) systems and computational phase equilibria: Crystallization of MgAl₂O₄ spinel. *Calphad* 2007, *31*, 428–437. [CrossRef]
- Park, J.H. Formation of CaZrO₃ at the interface between CaO-SiO₂-MgO-CaF₂(-ZrO₂) slags and magnesia refractories: Computational and experimental study. *Calphad* 2007, *31*, 149–154. [CrossRef]
- 26. Bale, C.W.; Chartrand, P.; Degterov, S.; Eriksson, G.; Hack, K.; Mahfoud, R.B.; Melançon, J.; Pelton, A.; Petersen, S. FactSage Thermochemical Software and Databases. *Calphad* **2002**, *26*, 189–228. [CrossRef]
- 27. Cong, W.; Zhang, J. Fine-tuning Weld Metal Compositions via Flux Optimization in Submerged Arc Welding: An Overview. *Acta Metall. Sin.* **2022**, *57*, 1126–1140. [CrossRef]
- Chai, C.; Eagar, T. Prediction of Weld-metal Composition during Flux-shielded Welding. J. Mater. Energy Syst. 1983, 5, 160–164. [CrossRef]
- 29. Chai, C.; Eagar, T. Slag-metal Equilibrium during Ssubmerged Arc Welding. Metall. Trans. B 1981, 12, 539–547. [CrossRef]
- Zhang, J.; Wang, C.; Coetsee, T. Assessment of Weld Metal Compositional Prediction Models Geared Towards Submerged Arc Welding: Case Studies Involving CaF₂-SiO₂-MnO and CaO-SiO₂-MnO Fluxes. *Mater. Trans. B* 2021, *52*, 2404–2415. [CrossRef]
- Indacochea, J.; Blander, M.; Shah, S. Submerged Arc Welding: Evidence for Electrochemical Effects on the Weld Pool. Weld. J. 1989, 68, 11–14.
- 32. Burck, P.; Indacochea, J.; Olson, D. Effects of Welding Flux Additions on 4340 Steel Weld Metal Composition. *Weld. J.* **1990**, *3*, 115–122.
- Dallam, C.; Liu, S.; Olson, D. Flux Composition Dependence of Microstructure and Toughness of Submerged Arc HSLA Weldments. Weld. J. 1985, 64, 140–151.
- Zhang, J.; Coetsee, T.; Dong, H.; Wang, C. Element Transfer Behaviors of Fused CaF₂-SiO₂-MnO Fluxes under High Heat Input Submerged Arc Welding. *Metall. Mater. Trans. B* 2020, *51*, 885–890. [CrossRef]
- 35. Mitra, U.; Eagar, T. Slag-metal Reactions During Welding: Part II. Theory. Metall. Trans. B 1991, 22, 73-81. [CrossRef]
- Zhang, J.; Coetsee, T.; Wang, C. Element Transfer Behaviors of Fused CaF₂-SiO₂ Fluxes Subject to High Heat Input Submerged Arc Welding. *Metall. Mater. Trans. B* 2020, *51*, 16–21. [CrossRef]
- Zhang, J.; Coetsee, T.; Dong, H.; Wang, C. Element Transfer Behaviors of Fused CaF₂-TiO₂ Fluxes in EH36 Shipbuilding Steel during High Heat Input Submerged Arc Welding. *Metall. Mater. Trans. B* 2020, *51*, 1953–1957. [CrossRef]