



Communication

Element Transfer Behaviors of Fused $\text{CaF}_2\text{-TiO}_2$ Fluxes in EH36 Shipbuilding Steel During High Heat Input Submerged Arc Welding

JIN ZHANG, THERESA COETSEE, HONGBIAO DONG, and CONG WANG

Fused $\text{CaF}_2\text{-TiO}_2$ fluxes are developed and applied on EH36 shipbuilding plates under high heat input submerged arc welding. Transfer behaviors of O and major alloying elements are systematically investigated. TiO_2 contributes to O gain in the weld pool, but leads to concurrent losses of Si, Mn, and C *via* deoxidation and decarburization reactions. Transfer of Ti to the weld metal is suppressed due to improved flux O potential and chemical interaction between CaF_2 and TiO_2 .

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Submerged arc welding (SAW) is widely applied for the welding of thick steel grades due to its inherently high deposition rate.^[1] During SAW, no shielding gas is required as the weld pool is protected by a layer of molten slag and granular flux from atmospheric contamination.^[2]

Flux is the primary source of O for weld metal (WM), and flux basicity is an indirect indication of the flux O potential.^[3–6] Generally, higher flux basicity means lower flux O potential and better mechanical properties, especially low-temperature toughness.^[7,8] Among several flux categories, basic-fluoride fluxes are widely

applied to achieve excellent mechanical properties as the addition of CaF_2 improves basicity and minimizes flux O potential.^[5,9–13]

In recent years, to further improve mechanical properties or counter toughness deterioration of the weld under high heat input welding, TiO_2 , a typical acicular ferrite (AF) promoting component, is introduced into basic-fluoride fluxes.^[11,14–16] As such, Ti and O are transferred to the WM *via* chemical reactions in the arc and weld pool zones.^[11,13,17] Subsequently, Ti-containing inclusions are dispersed, AF formation is facilitated, and the enhancement of mechanical properties of the weldment is anticipated.^[18]

When TiO_2 -bearing basic-fluoride fluxes are applied, it is essential to understand the roles of TiO_2 in the control of WM compositions to ultimately achieve desired mechanical properties.^[11,14,19] Several authors investigated the effects of TiO_2 content in varying basic-fluoride fluxes over a wide range of WM compositions. For instance, Kohno *et al.*^[14] developed $\text{CaF}_2\text{-SiO}_2\text{-BaO-Al}_2\text{O}_3\text{-TiO}_2$ fluxes, which could transfer Ti and O to the WMs *via* the reduction of TiO_2 in the fluxes, concluded that the Ti content in the WM increased with lower flux potential. Roy *et al.*^[20] investigated the influence of TiO_2 content on WM compositions employing $\text{CaF}_2\text{-SiO}_2\text{-MgO-Al}_2\text{O}_3\text{-MnO-TiO}_2$ fluxes, and found that the Ti level of the WM was promoted with TiO_2 addition from 0 to 12.5 wt pct. Zhang *et al.*,^[11] on the other hand, performed SAW using $\text{CaF}_2\text{-SiO}_2\text{-Al}_2\text{O}_3\text{-MgO-TiO}_2$ fluxes with varying TiO_2 addition from 1 to 16 wt pct, and revealed that WM Ti content reached a maximum when 6 wt pct TiO_2 -containing flux was applied.

However, the studies reviewed above only considered WM's change in final compositions, in which the elemental contribution from the flux is not quantified and evaluated. In SAW engineering, a namely Δ value is widely applied to express the element transfer between flux and WM: a positive Δ value indicates flux contribution to elemental gain for the WM, whereas a negative Δ value means corresponding elemental loss for the WM.^[5,7,9,10,12,16,21–24] Such quantitative measure is essential to understand the transfer mechanisms between flux and WM, and to provide guidelines matching appropriate welding consumables.^[9,12,25] Influences of SiO_2 , MnO, and CaO on the element transfer behaviors have been extensively investigated,^[9,10,12,21,22,26] nonetheless, the role of TiO_2 on this subject remains at large.

This study focuses on the influence of TiO_2 on WM composition control using TiO_2 -bearing basic-fluoride fluxes. It is well known that oxides tend to provide O₂ *via* decomposition in the welding arc, improve weld pool O level, and influence the transfer of alloying elements.^[2,13] Therefore, only CaF_2 , which intrinsically exerts no O potential for the weld, is selected as extra component to exclude such effects.^[2,13,25–27]

JIN ZHANG is with the School of Metallurgy, Northeastern University, Shenyang 110819, China. THERESA COETSEE is with the Department of Materials Science and Metallurgical Engineering, University of Pretoria, Pretoria, 0002, South Africa. HONGBIAO DONG is with School of Metallurgy, Northeastern University and also with the Department of Engineering, University of Leicester, Leicester LE1 7RH, UK. CONG WANG is with School of Metallurgy, Northeastern University and also with the State Key Laboratory of Rolling and Automation, Northeastern University, Shenyang 110819, China. Contact e-mail: wangc@smm.neu.edu.cn

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Additionally, CaF₂ is an effective modifier for the slag physical properties, especially melting point and viscosity.^[9,28] In this regard, binary CaF₂-TiO₂ fluxes are designed, and elemental transfer between flux and WM is quantified. Furthermore, probable reactions that govern the transfer of O, Ti, Si, Mn, and C are investigated and evaluated from thermodynamic perspectives.

It is accepted that a flux must have a melting range lower than the WM so that the molten flux solidifies after the molten WM does.^[7] Also, it is reported that flux should have adequate viscosity (higher than 0.2 Pa·s at 1673 K) to cover and protect the weld pool from atmospheric gases.^[7,29] Based on these criteria, phase diagram and viscosity data of CaF₂-TiO₂ melts are referenced,^[30-32] and five CaF₂-TiO₂ binary fluxes were designed with formulas summarized in Table I.

Fluxes were prepared by the fused method.^[7] Reagent grade CaF₂ and TiO₂ powders were selected as raw materials, and the fluxes were melted at 1823 K in graphite crucibles following the procedures stated in our previous studies.^[9,12] The fluxes were baked at 973 K for

2 hours to remove moisture and exclude C contamination before welding.^[21,22] Evaporation of the fluoride species from the melt fluxes was expected,^[28] and the losses of CaF₂ and TiO₂ determined by X-Ray Fluorescence (XRF, model S4 Explorer) were within 5 pct of their initial compositions, similar to our previous studies.^[9,12]

EH36, a typical shipbuilding steel, was selected as the base metal (BM). Lincoln Electric Power Wave AC/DC 1000 SD (Lincoln Electric, China) was employed as the welding equipment. Bead-on-plate double-wires (DC-850 A/32 V for electrode forward, AC-625 A/36 V for electrode backward, 60 kJ/cm) SAW was performed on 24 mm thickness BM, and the welding speed was maintained at 500 mm/min. The chemical composition analysis methods for BM, electrode, and WM are stated elsewhere.^[9,12,26] The compositions of BM and electrode are shown in Table II.

The welds were cross-sectioned, polished, and etched by 4 wt pct nital solution to determine WM geometries for the calculation of WM nominal composition (composition considering only simple physical mixing of BM and electrode).^[9,12,21,22] As is mentioned previously, the Δ value is used to quantify the element transfer between flux and WM. The calculation methods of nominal composition and Δ value have been stated in previous studies.^[12,21,22] Analytical compositions (with subscript 'A'), nominal compositions (with subscript 'N'), and Δ values of WMs are given in Table III.

First, the transfer of O is investigated as it fundamentally dictates the transfer of alloying elements.^[9,17,33] ΔO values, which reflect the O potentials of the fluxes, are plotted in Figure 1 as a function of TiO₂ content. As

Table I. Formulas of Fluxes Employed (Weight Percent)

| Fluxes | TiO ₂ | CaF ₂ |
|--------|------------------|------------------|
| F-1 | 20 | 80 |
| F-2 | 25 | 75 |
| F-3 | 30 | 70 |
| F-4 | 35 | 65 |
| F-5 | 40 | 60 |

Table II. Chemical Compositions of BM and Electrode (Weight Percent)

| | C | Si | Mn | Ti | Nb | Ni | Cr | O |
|-----------|-------|-------|-------|-------|-------|-------|-------|-------|
| EH36 | 0.052 | 0.142 | 1.540 | 0.010 | 0.013 | 0.075 | 0.028 | 0.003 |
| Electrode | 0.127 | 0.049 | 1.650 | 0.010 | 0.004 | 0.009 | 0.030 | 0.003 |

Table III. Chemical Compositions of WMs (Weight Percent)

| Weld metals | WM-1 | WM-2 | WM-3 | WM-4 | WM-5 |
|-------------------|---------|---------|---------|---------|---------|
| Fluxes | F-1 | F-2 | F-3 | F-4 | F-5 |
| (O) _A | 0.012 | 0.015 | 0.015 | 0.019 | 0.022 |
| (O) _N | 0.003 | 0.003 | 0.003 | 0.003 | 0.003 |
| ΔO | 0.009 | 0.012 | 0.012 | 0.016 | 0.019 |
| (Ti) _A | 0.019 | 0.023 | 0.041 | 0.039 | 0.037 |
| (Ti) _N | 0.010 | 0.010 | 0.010 | 0.010 | 0.010 |
| ΔTi | 0.009 | 0.013 | 0.031 | 0.029 | 0.027 |
| (Si) _A | 0.063 | 0.061 | 0.070 | 0.057 | 0.051 |
| (Si) _N | 0.094 | 0.097 | 0.103 | 0.100 | 0.097 |
| ΔSi | - 0.031 | - 0.036 | - 0.033 | - 0.043 | - 0.046 |
| (Mn) _A | 1.412 | 1.413 | 1.399 | 1.374 | 1.384 |
| (Mn) _N | 1.596 | 1.594 | 1.586 | 1.589 | 1.593 |
| ΔMn | - 0.184 | - 0.181 | - 0.187 | - 0.215 | - 0.209 |
| (C) _A | 0.075 | 0.075 | 0.066 | 0.069 | 0.065 |
| (C) _N | 0.090 | 0.089 | 0.084 | 0.086 | 0.088 |
| ΔC | - 0.015 | - 0.014 | - 0.018 | - 0.017 | - 0.023 |

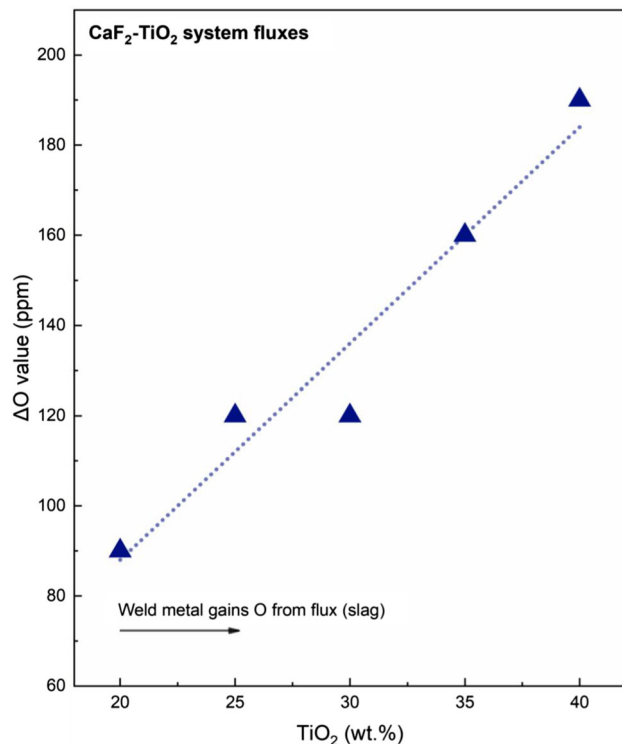


Fig. 1— ΔO values as a function of TiO_2 content in fluxes.

shown in Figure 1, ΔO value increases from 90 to 190 ppm when the TiO_2 level is improved from 20 to 40 wt pct.

Chai *et al.*^[13,27] and Mitra *et al.*^[17,34] reported that TiO_2 was susceptible to decomposition, promoted the release of O_2 , and improved the O level of the droplets and weld pool in the presence of the welding arc, although the decomposition mechanisms were not fully understood. Mitra *et al.*^[17] and Lau *et al.*^[3] concluded that the O uptake from the flux was governed by the level of p_{O_2} in the plasma.^[22] Thus, it is deduced that p_{O_2} is promoted with increasing TiO_2 addition owing to higher extent of oxide decomposition, similar to the case when binary CaF_2-SiO_2 and CaF_2-MnO fluxes were applied.^[9,10,13] It should be noted that Chai *et al.*^[13] also investigated the O potential of binary CaF_2-TiO_2 flux with one formula; however, the dilution effects of BM and electrode were not taken into account, and the compositional contribution from the flux (ΔO) was not quantified.

Compositions of Ti as a function of TiO_2 variation in the flux are plotted in Figure 2. Ti is transferred to the WM with TiO_2 addition in the flux according to positive Δ values observed. Zhang *et al.*^[11] and Erokhin^[35] reported that Ti was transferred from slag to weld pool *via* Reactions [1] and [2] at the slag-metal interface in SAW.

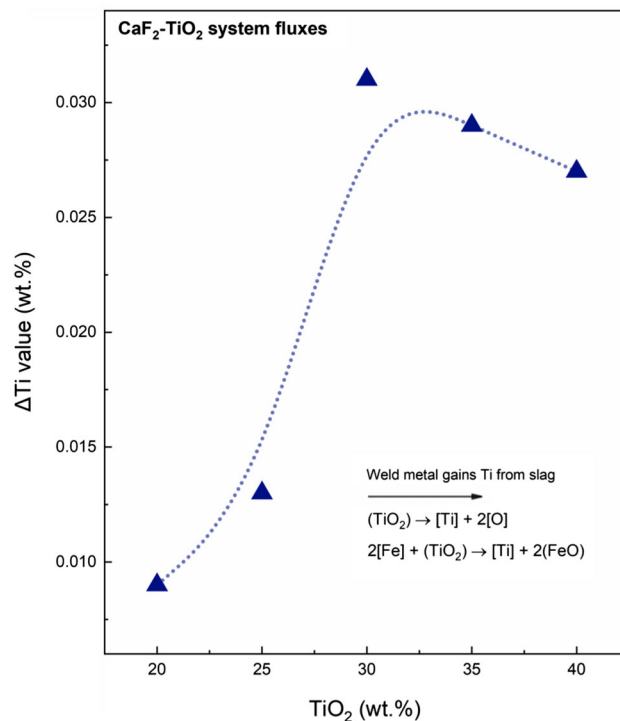
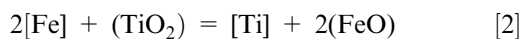
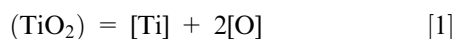
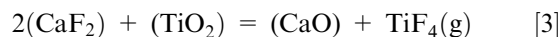


Fig. 2— ΔTi values as a function of TiO_2 content in fluxes.

From an observation in Figure 2, when the TiO_2 content in the flux is lower than 30 wt pct, ΔTi increases from 0.009 to 0.031 wt pct with TiO_2 addition. However, when the TiO_2 content exceeds 30 wt pct, transfer of Ti is suppressed. As is discussed above, the O content in the weld pool increases with higher TiO_2 content. Also, Indacochea *et al.*^[22] concluded that the activity of FeO at the slag-metal interface was proportional to the weld pool O level. Therefore, the increase of O and FeO activity levels suppresses the transfer efficiency of Ti by driving both Reactions [1] and [2] to the left sides. Such reduction of Ti transfer efficiency with higher flux O potential was also observed in the work of Kohnno *et al.*^[14] and Zhang *et al.*^[11] when TiO_2 -bearing basic-fluoride fluxes were employed.

Additionally, Devletian *et al.*^[36] and Sikorski^[37] reported the possibility of TiF_4 gas evolution in welding processes. Thus, the chemical interaction between CaF_2 and TiO_2 (Reaction [3]), which may promote the reduction of Ti *via* the formation of TiF_4 gas, should be considered.^[28]



It is noted that precise information on the gas compositions in the plasma is still not available, as is reviewed by Sengupta *et al.*^[1] To quantitatively analyze the influence of Reaction [3] on the loss of Ti, the precise partial pressure of TiF_4 in the plasma is anticipated.^[25]

To further confirm the element transfer mechanisms above, compositional changes between slags and their corresponding fluxes, which are defined as δ values, are quantified and illustrated in Figure 3.^[9,12] The observed

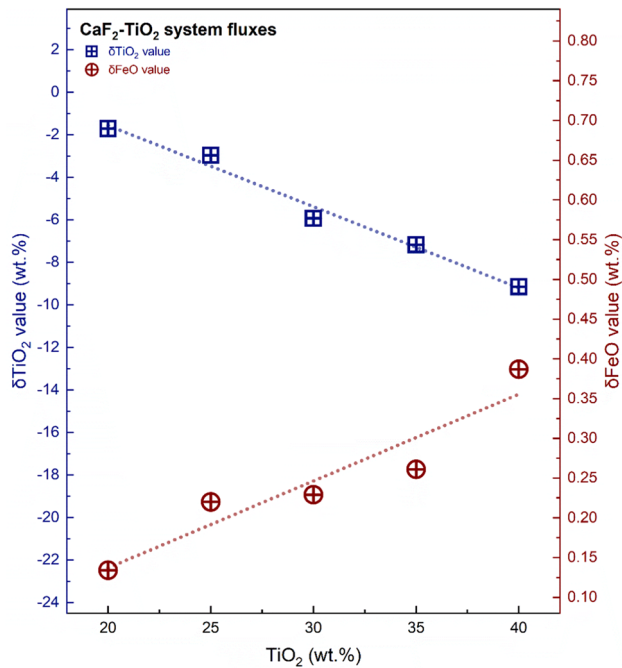
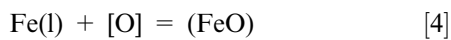


Fig. 3— δ values of TiO_2 and FeO as a function of TiO_2 content in fluxes.

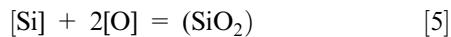
negative δTiO_2 values indicate that Ti can be transferred to the WMs by the reduction of TiO_2 in the fluxes.^[14] By comparing Figures 2 and 3, the magnitude of δTiO_2 generally increases with higher level of TiO_2 addition, although the ΔTi value undergoes a spike at 30 wt pct TiO_2 . The difference of the changing trends between the magnitude of δTiO_2 and ΔTi implies that Ti is lost to the gas phase, most probably *via* Reaction [3].^[28,36,37]

Furthermore, FeO was analyzed in the slags. It is reported that Fe is oxidized at the slag-metal interface *via* Reaction [4].^[17]



Reaction [4] generally proceeds only forward, as is concluded by Mitra *et al.*^[17] As shown in Figure 3, δFeO value is directly proportional to the concentration of TiO_2 due to improved O level in the weld pool,^[17] and Reaction [4] is shifted to the right side, which is consistent with our previous conclusions.^[9,12]

Si and Mn are basic elements and deoxidizers for submerged arc welded metal.^[27] Si and Mn are lost to slag *via* Reactions [5] and [6] as no SiO_2 and MnO are contained in the fluxes initially,^[9] which is reflected by negative ΔSi and ΔMn values illustrated in Figure 4.



With the increase of TiO_2 content from 20 to 40 wt pct, the loss of Si increases from 0.031 to 0.046 wt pct, and the loss of Mn increases from 0.181 to 0.215 wt pct,

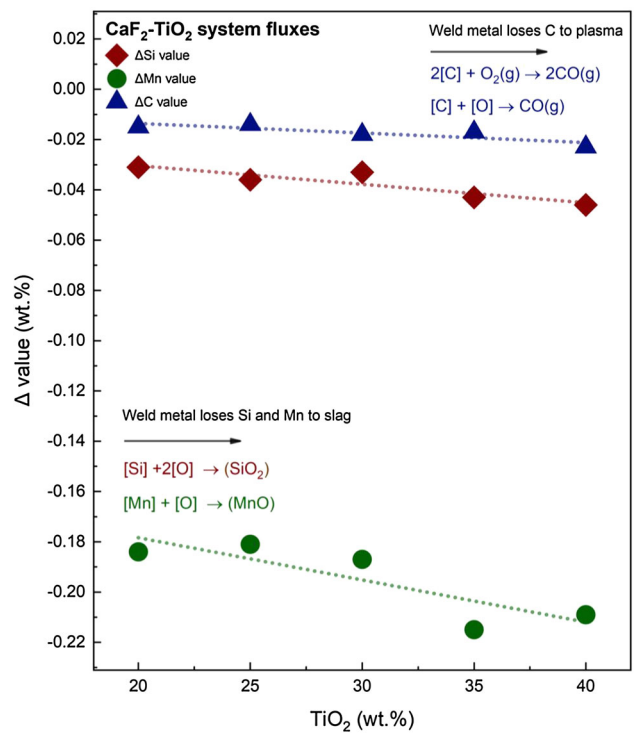
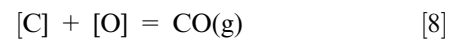


Fig. 4—Values of ΔSi , ΔMn , and ΔC as a function of TiO_2 content in fluxes.

due to higher O level in the weld pool, which drives both Reactions [5] and [6] to the right sides.

Decarburization tends to occur due to O_2 generated in the plasma and O uptake in the weld pool from the flux, and C is lost at the plasma-metal interface *via* Reactions [7] and [8].^[22,25] The contribution of flux to the extent of decarburization (ΔC) is quantified and shown in Figure 4.



Furthermore, the possibility of bubble nucleation under slag is investigated as it determines whether decarburization is feasible at the bubble-metal interface.^[22,25,38] The bubble nucleation possibility under silicate-network based slags has been investigated; however, similar studies involving titanate-network based fluxes remain scarce.^[25] In this study, no significant bubble is observed under detached-slag surfaces, possibly due to bubble nucleation being hindered by the large surface tensions of the slags.^[22,25] Therefore, it is expected that Reactions [7] and [8] are only possible at the plasma-metal interface for the present flux system.

In summary, by designing and employing fused $\text{CaF}_2\text{-TiO}_2$ binary fluxes, transfer behaviors have been quantified, and possible mechanisms have been evaluated from thermodynamic perspectives. The following conclusions can be drawn:

1. TiO₂ tends to decompose, release O₂, and ultimately improve the O level of the WM.
2. Ti is transferred to the weld pool *via* slag-metal reactions. When the TiO₂ addition level in the flux is higher than 30 wt pct, the transfer of Ti to the WM is suppressed due to improved flux O potential and chemical interaction between CaF₂ and TiO₂.
3. Si and Mn in the weld pool are oxidized at the slag-metal interface. C is lost *via* decarburization reactions, which likely occur at the plasma-metal interface.

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