Effect of NaF and CaO/SiO₂ on the Hydrogen Dissolution in the CaO–SiO₂–FeOt Based Flux System

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The compositional effect of NaF and CaO/SiO₂ on the hydrogen solubility in the NaF–CaO–SiO₂–FeOt welding flux system at 1 823 K is presented. At a CaO/SiO₂ of 1.3, higher NaF decreased the hydrogen solubility and at a CaO/SiO₂ of 1.5, higher NaF had relatively little effect on the hydrogen solubility in the flux. The hydrogen solubility with CaO/SiO₂ showed a parabolic behavior showing a minimum near unit basicity and increasing with higher basicity. FTIR (Fourier transform infra red) and Raman spectroscopy of as-quenched flux samples showed the addition of NaF and higher CaO/SiO₂ depolymerized the flux structure. At low and intermediate basicities from 0.9 to 1.3, higher NaF decreased the incorporated hydroxyl sites of Si(OH) and FeO(OH), which correlates well to lower hydrogen values.

KEY WORDS: NaF; CaO/SiO₂; hydrogen solubility; welding flux; FTIR; Raman.

1. Introduction

The needs of ultra-light highly formable steels for maximum fuel efficiency have brought significant developments in advanced high strength steels (AHSS). And although considerable improvements in bulk properties have been realized, there has been comparatively less focus on improving the conditions of the weld joints and the control of diffusible hydrogen. In recent work, So et al. have shown that 800 MPa and higher steels have shown particular vulnerability at the weld joints due to hydrogen delayed cracking. Weld joints are seriously affected from excess hydrogen, causing hydrogen induced cracking, embrittlement, and pores in steels. High strength steels with as much as 10 ppm hydrogen can show decreased physical strength and performance. Therefore controlling the hydrogen contents to sub ppm levels is required to achieve the designed strength and weld-ability of these new grades of high strength steels. To achieve these sub ppm levels, a high hydrogen capacity of the welding flux is required. Industrial welding fluxes designed for high hydrogen capacity is typically CaO based fluxes with various oxides and halides. However, there has been relatively little systematic work done on the hydrogen dissolution at the weld joints in particular regarding these welding type fluxes.

Previous work published on the solubility of hydrogen in the CaF₂–CaO–SiO₂–FeOt flux system showed CaF₂ additions at high basicity increased the hydrogen content. The structural analysis with FTIR showed a decrease in the FTIR transmittance bands for NBO/Si=1 and Si–OH bonds with higher CaF₂ suggesting a depolymerization of the slag structure.

The hydrogen solubility was affected by the flux composition, temperature, and apparent basicity (CaO/SiO₂ mass ratio), where basicity was a major factor in hydrogen dissolution. According to Russell and Fukushima et al., the subsequent dissolution of hydrogen in steelmaking slags from wet gases suggested different mechanisms are involved dependent on the slag composition. For an acidic slag of low basicity, the hydrogen dissolves in slag as an incorporated hydroxyl according to reaction (1) and for a basic slag, the hydrogen dissolves as a free-hydroxyl according to reaction (2).

Incorporated hydroxyl : Si–O–Si + H₂O = 2Si–OH ... (1)
Free hydroxyl : H₂O + O²− = 2OH⁻ ............. (2)

Thus, the hydrogen dissolution in the incorporated hydroxyl mechanism can decrease with higher basicity as the activity of the Si–O–Si incorporation sites decrease and in the free-hydroxyl mechanism can increase with higher basicity as the activity of O²⁻ increase.

In this study, the hydrogen solubility in the NaF–CaO–SiO₂–FeOt flux system has been studied. In particular, the effect of NaF and CaO/SiO₂, which can be the major constituents in the formulation of new welding fluxes applied to ultra-low hydrogen FCAW (flux cored arc welding), was investigated. Due to the varying flux composition and corresponding oxygen partial pressures, there is a variation in the Fe²⁺ and Fe³⁺ distribution in the flux. Thus, the distribution of the FeO₃ as Fe₂O₃ and FeO were also later accounted for in determining the hydrogen dissolution behavior. In addition, the hydrogen dissolution behavior and the effects of compositional variation in the flux were correlated to the
flux structure using FTIR (Fourier transform infra red) and Raman spectroscopy.

2. Experimental Method and Procedure

2.1. Sample Preparation and Hydrogen Analysis

Reagent grade NaF, CaO, SiO₂ and FeO were used to prepare the sample. 3.5 g of the specimen were premelted at 1 823 K under 0.2 L/min of argon gas in a Pt crucible for 5 h to obtain a homogeneous master slag. Pre and post experimental chemical composition of the samples were determined from XRF (S4 Explorer, Bruker AXS GmbH Karlsruhe, Germany) and are listed in Table 1. The distribution of Fe²⁺ and Fe³⁺ was analyzed by the K₂Cr₂O₇ titration method (JIS M 8212:2005). Due to fluorine vaporization during the experiment, the post experimental compositions were taken to be the experimental compositions after thermo-chemical equilibrium was obtained. Figure 1 shows a schematic of the experimental apparatus and the main components. 0.2 L/min of argon flows inside the stainless inlet tube and passes through a column of water maintained at 333 K. An H₂O partial pressure of approximately 0.2 atm leaves the humidifying vessel. To prevent condensation and changes in the H₂O partial pressure at the hot zone of the furnace, the outline lines between the humidifier and the furnace were externally heated to 343 K using an electrical resistance heating tape. The fully saturated gas is injected into the reaction tube situated within the Kanthal vertical resistance furnace. The furnace temperature was calibrated with a B-type reference thermocouple and controlled within ±3 K using a PID (proportional integral differential) controller. The sample was equilibrated for 5 h at 1 823 K to ensure

| No.      | Pre-experimental composition (mass%) | Post-experimental composition (mass%) | H (mass ppm) | CaO/SiO₂ (Pre/Post) |
|----------|--------------------------------------|---------------------------------------|--------------|---------------------|
|          | NaF  CaO  SiO₂  FeO                  | NaF  CaO  SiO₂  FeO                  |              |                     |
|          | (mass)  (mass)  (mass)  (mass)       | (mass)  (mass)  (mass)  (mass)       |              |                     |
| NCSF1    | 0  46.4  38.6  15                      | 0.0  46.8  35.3  –                 | –            | 35.6  2.19           | 1.2/1.33  |
| NCSF2    | 3  44.7  37.3  15                      | 3.6  44.7  34.9  4.74            | 11.23        | 26.5  3.26           | 1.2/1.28  |
| NCSF3    | 6  43.1  35.9  15                      | 4.9  44.2  34.2  4.78            | 11.34        | 21.3  0.76           | 1.2/1.29  |
| NCSF4    | 9  41.5  34.6  15                      | 5.8  43.8  33.4  4.56            | 11.35        | 17.7  1.23           | 1.2/1.31  |
| NCSF5    | 6  29.6  49.4  15                      | 6.3  30.4  46.6  –                | –            | 22.8  2.83           | 0.6/0.65  |
| NCSF6    | 6  35.1  43.9  15                      | 6.2  36.4  41.5  5.90            | 10.18        | 19.0  0.4            | 0.8/0.88  |
| NCSF7    | 6  39.5  39.5  15                      | 5.3  41.1  37.4  4.31            | 11.86        | 16.1  0.06           | 1.0/1.10  |
| NCSF8    | 6  48.6  40.5  5                       | 4.7  47.6  42.1  1.16            | 4.83         | 14.6  0.53           | 1.2/1.13  |
| NCSF9    | 6  45.8  38.2  10                      | 4.0  47.7  37.0  1.99            | 9.21         | 17.6  4.02           | 1.2/1.29  |
| NCSF10   | 0  49.6  35.4  15                      | 0.0  49.9  32.1  –                | –            | 25.0  0.28           | 1.4/1.56  |
| NCSF11   | 3  47.8  34.2  15                      | 2.7  48.5  31.7  –                | –            | 27.9  0.99           | 1.4/1.53  |
| NCSF12   | 8  44.9  32.1  15                      | 4.5  47.7  30.8  –                | –            | 24.3  2.69           | 1.4/1.55  |
| NCSF13   | 6  48.6  30.4  15                      | 5.7  49.7  28.7  –                | –            | 25.2  2.55           | 1.6/1.74  |
| NCSF14   | 6  50.8  28.2  15                      | 4.8  51.9  26.5  –                | –            | 27.7  2.16           | 1.8/1.96  |

Fig. 1. Experimental set-up with humidifying vessel.
thermodynamic equilibrium of the flux (slag) is reached for hydrogen dissolution. Preliminary experiments have shown 5 h to be sufficient in obtaining a thermo-chemical equilibrium state. After equilibration, the sample was quickly removed from the hot zone of the furnace and quenched in liquid nitrogen. XRD analysis in Fig. 2 shows no characteristic diffraction peaks, but a broad band typical of a fully amorphous sample. As-quenched samples, were kept inside an argon gas purged container and analyzed for hydrogen within 48 h. Hydrogen was analyzed using a LECO RH-600 hydrogen analyzer utilizing a thermal conductivity detector (LECO, MI, USA).

2.2. Flux Structure Analysis Using FTIR Spectroscopy

To identify the flux structure, FTIR (Spectra100; Perkin-Elmer, Shelton CT, USA) spectroscopy was done on as-quenched flux samples from 1823 K. Sample aliquots for FTIR analysis was produced from 2 mg of flux sample, mixed with 200 mg of KBr in an agate mortar and pelletized to 10 mm diameter cylindrical tablets. The FTIR spectra region from 4000 to 400 cm$^{-1}$ was typically concentrated between 1400–400 cm$^{-1}$, where the silicate symmetric stretching, asymmetric bending, and rocking vibration of the Si–O–Si bonding are focused. The details of the aforementioned transmittance bands have been provided in detail elsewhere.6)

2.3. Flux Structure Analysis Using Raman Spectroscopy

A more quantitative analysis is possible using Raman spectroscopy (PD-RSM300; Photon Design, Japan) with a 514 nm blue laser. Similar to the FTIR, the various silicate peaks of the Raman exists in the range between 800–1200 cm$^{-1}$. The silicate bond vibrations of the present flux system are both IR and Raman active. Figure 3 is a typical Raman spectra obtained from a sample with 0 mass% NaF and 16 mass% FeO$_2$ at a fixed CaO/SiO$_2$ mass ratio of 1.3. The Peak Fit V4 software (Systat Software Inc, Chicago IL, USA) was used to deconvolute the spectra. For FeO$_2$ containing slags, Raman peaks for the $\delta$-FeO(OH) and $\gamma$-FeO(OH) located near 1120 cm$^{-1}$ and 1160 cm$^{-1}$, respectively, have also been considered in the deconvolution of the spectra.

3. Results and Discussion

3.1. Effect of NaF on the Hydrogen Solubility at Fixed CaO/SiO$_2$

Figure 4 shows the hydrogen content in the NaF–CaO–SiO$_2$–FeO$_2$ system as a function of NaF at fixed apparent basicity (CaO/SiO$_2$) of 1.3 and 1.5 at 1823 K. The hydrogen solubility in the slag decreases with higher NaF at CaO/SiO$_2$ of 1.3, but NaF additions is comparably ineffective at higher CaO/SiO$_2$ of 1.5. According to the work by Kim and Sohn,NaF was found to be a network modifying flux, which interacts with the bridged oxygen of the silicate and aluminate structures to depolymerize the slag and increase the activity of O$^{2-}$. At CaO/SiO$_2$ of 1.3, the slag still contains complex network structures with bridged oxygen (O$^2$), which can react with the network breaking NaF, depolymerizing the slag. If the incorporated hydroxyl mechanism significantly contributes to the overall hydrogen solubility, an increase in the free oxygen ions (O$^{2-}$) due to the depolymerization of the slag structure from higher NaF additions can result in lower hydrogen. This depolymerization is qualitatively observed from the FTIR spectra provided in subsequent sections. At CaO/SiO$_2$ of 1.5, the slag is already significantly depolymerized due to the CaO component of the slag and the addition of NaF has comparatively little effect in

![Fig. 2. XRD analysis of NaF–CaO–SiO$_2$–FeO$_2$ flux sample as-quenched in liquid N$_2$ from 1823 K.](image)

![Fig. 4. Hydrogen solubility in the NaF–CaO–SiO$_2$–FeO$_2$ flux as a function of NaF content at 1823 K and fixed CaO/SiO$_2$ of 1.3 and 1.5.](image)
Increasing the amount of free oxygen ions. Thus additions of NaF at higher basicity seem to be negligible with regards to increasing hydrogen dissolution into slag.

3.2. Effect of NaF on the Slag Structure

In Fig. 5, higher NaF content increased the trough depth of the simple silicate structures of NBO/Si ratio of 4 located between 880–850 cm⁻¹. The characteristic FTIR transmittance troughs were identified using established literature references provided in Table 2. This increased depth in the trough suggests a depolymerization with higher NaF additions. In addition, the intensity of the Si–O–Si rocking band, which exist near 500 cm⁻¹, decrease with higher NaF content from 0 to 5.8 mass% suggesting depolymerization of the slag. For a more semi-quantitative analysis of the depolymerization, Raman spectroscopy were performed on the as-quenched slag samples. Since NaF depolymerizes the slag and increases the free oxygen activity resulting in lower hydrogen solubility of the 1.3 basicity slag, it seems that the incorporated hydroxyl as expressed by reaction (1) is significant. Figure 7 shows the percent of the various structural units of the slag melt as a function of NaF including NBO/Si (non bridged oxygen per silicon atom) of 1, 2 and 3 obtained from integrating the deconvoluted peaks of the Raman spectra in Fig. 6. Similar to the FTIR analysis, the peaks of the Raman spectra were identified using the aforementioned established references in Table 2. For the present silicates, the slag samples show FTIR transmittance troughs and Raman peaks at comparable wavelengths, which seem to suggest that the slag is both IR and Raman active. The sum of the NBO/Si of 1 and 3 decreases, but the NBO/Si of 2 increases with higher NaF. According to Mysen et al.,

\[
Q^1(NBO/Si=3) + Q^1(NBO/Si=1) \rightarrow Q^2(NBO/Si=2) + Q^2(NBO/Si=2) \] ........................ (3)

Furthermore, Fig. 7 shows the presence of the Si–OH and the

![Fig. 5. FTIR analysis of as-quenched flux samples at various NaF content and fixed CaO/SiO₂ of 1.3.](image)

![Fig. 6. Deconvoluted Raman spectra of the NaF–CaO–SiO₂–16 mass% FeOt flux for various NaF concentrations at fixed CaO/SiO₂ of 1.3.](image)

![Fig. 7. The percent of structural units as a function of NaF content at fixed CaO/SiO₂ of 1.3 obtained from the integration of the deconvoluted Raman spectra of as-quenched flux samples from 1823 K.](image)

Table 2. FTIR and Raman reference data from published literature.

| Mode                        | Species     | Wavenumber (cm⁻¹) | Reference       |
|-----------------------------|-------------|-------------------|-----------------|
| Asymmetric stretching       | NBO/Si=0    | 1060              | [10–12]         |
|                            |             | 1090              |                 |
|                            | NBO/Si=1    | 1100              |                 |
|                            | NBO/Si=2    | 950–980           | [10–11,14]      |
|                            | NBO/Si=3    | 900–920           |                 |
|                            | NBO/Si=4    | 850–880           |                 |
| Symmetric stretching        | Si–OH       | 950–980           | [8,10,11,14]    |
| Rocking vibration           | Si–O–Si     | 400–550           | [8]             |
| –OH Stretching vibration    | δ–FeO(OH)   | 1120              | [11,12]         |
|                            | γ–FeO(OH)   | 1160              |                 |
FeO(OH) incorporated-hydroxyl bonding, which decreases with NaF additions, suggesting lower hydrogen dissolution into slag with higher NaF to be a result of this decrease in the incorporated hydroxyl sites within the flux.

### 3.3. Effect of CaO/SiO$_2$ and Fe$_2$O$_3$ on the Hydrogen Solubility at Fixed NaF

Previous work on the hydrogen solubility of CaF$_2$–CaO–SiO$_2$–FeO$_x$ fluxes indicated significant variations as a function of the CaO/SiO$_2$ ratio, where the dominant hydrogen dissolution mechanism at low basicity is incorporated hydroxyl and at high basicity is free hydroxyl. Figure 8 shows a parabolic behavior of the hydrogen solubility as a function of CaO/SiO$_2$ in the NaF–CaO–SiO$_2$–FeO$_x$ flux system with slightly varying NaF content from 4.8 to 6.3 mass%.

The slight variation in NaF should have relatively little impact on the overall trend and hydrogen content in slag. From a CaO/SiO$_2$ of 0.65 to 1.1 or low basicity, the hydrogen solubility in the flux decreases showing a minimum and at higher basicity of 1.1 to 1.96, the hydrogen content in slag increases. Thus, in the acidic region, the dominant mechanism of an incorporated hydrogen results in a decrease of the hydrogen content as the basicity increases according to the aforementioned reaction (1) and in the basic region of the slag, hydrogen dissolution increases with higher basicity due to increased O$^{2-}$ activity following the aforementioned reaction (2). Considering the availability of the incorporated hydroxyls of Si–OH and FeO(OH) for the basicity of 1.3 and the decrease in the hydrogen dissolution in slag with higher NaF additions, it may be speculated that this basicity is in the transition region between the acidic and basic slag system. If the relative amount of CaO, SiO$_2$, and NaF along with the initial addition of FeO of 16 mass% is taken into account, the overall composition was initially thought to be basic and higher NaF would generally increase the O$^{2-}$ activity of the slag resulting in higher hydrogen; only if the slag was basic. However, the existence of the Si–OH and FeO(OH) bonding in Fig. 7 and the decreasing trend with higher NaF at 1.3 basicity suggests that the present flux system is likely not to be purely basic, but in the intermediate region, where both incorporated and free hydroxyl’s coexist. If this was the case, the initial addition of 16 mass% FeO must have distributed into Fe$^{2+}$ and Fe$^{3+}$ due to the redox equilibrium set by the temperature and oxygen partial pressure with P$_{H_2O}$ of 0.2 atm. Thus, additional experiments to separately analyze the Fe$^{2+}$ and Fe$^{3+}$ were done. From the apparent basicity shown in Fig. 8, the basicity was extended to show the effects of both FeO and Fe$_2$O$_3$ on the hydrogen dissolution. The ratio has been divided with a constant of 0.78 and 0.38 relevant to the molecular weights of CaO to FeO and SiO$_2$ to Fe$_2$O$_3$. The shape of the parabolic wave in Fig. 9 seems to show a minimum between 1.1 to 1.2 and is comparable to the results presented in Fig. 8. The trend is similar to the effect of the apparent basicity and its mechanism should be comparable.

In addition, Fig. 10 shows the hydrogen dissolution with the addition of FeO in the NaF–CaO–SiO$_2$ containing flux at fixed CaO/SiO$_2$ of 1.3 and slight NaF variations from 4.0 to 4.9 mass%. The hydrogen solubility in the molten flux at 1823 K increases with higher FeO$_x$. From the aforementioned results on the effect of NaF at fixed CaO/SiO$_2$ of 1.3, both incorporated and free hydroxyls exist. According to the wet chemical analysis, the addition of FeO$_x$ distributes into FeO and Fe$_2$O$_3$ according to the oxygen partial pressure obtained from the flow of P$_{H_2O}$ of 0.2 atm. Considering that...
the amount of Fe$_2$O$_3$ increases with the addition of FeO, it seems likely that the overall increase in the hydrogen content is the result of an increase in the incorporated hydroxyl sites provided by FeO(OH). Thus as the acidic oxide of Fe$_2$O$_3$ increases, incorporated hydroxyl increases and the overall hydrogen dissolution in the flux can increase.

### 3.4. Effect of CaO/SiO$_2$ on the Slag Structure

Figure 11 shows the FTIR result as a function of CaO/SiO$_2$ ratio. The result shows NBO/Si ratio of 4 slightly increases with CaO/SiO$_2$. The trough depth representative of the simple silicate structures of NBO/Si=4 increases and the trough becomes wider with CaO/SiO$_2$ corresponding to an increase in this simple silicate structure suggesting the change in shape of the characteristic trough with CaO/SiO$_2$ is more pronounced compared to the effect of NaF in Fig. 5.

Similar to Fig. 7 in order to semi-quantitatively determine the depolymerization of the slag structure with higher CaO/SiO$_2$, Raman analysis of as-quenched slag samples were performed. Figure 13 shows the fraction of the major structural species of NBO/Si of 3, 2, Si–OH, and δ+γ-FeO(OH) as a function of the CaO/SiO$_2$ obtained from the integration of the deconvoluted Raman spectra shown in Fig. 12. According to the deconvolution results of the spectra, Si–OH, δ-FeO(OH), and γ-FeO(OH) decreased with higher CaO/SiO$_2$. In addition, the fractional sum of the NBO/Si=1 and NBO/Si=3 decreases with higher CaO/SiO$_2$ but the NBO/Si=2 increases indicating a depolymerization of the slag structure, which complements the results of the previous FTIR analysis. Thus, both the additions of NaF and increased basicity depolymerizes the slag, but depends on the amount of existing complex silicate structural units. As the highly basic oxide of CaO provides free oxygen ions (O$^-$), the addition of CaO breaks the bridged oxygen (O$_0$) bonds in the silicate structure decreasing the amount of complex structural units. When both CaO and NaF coexist, the CaO seems to be more effective in depolymerizing the slag and affecting the hydrogen dissolution.

### 4. Conclusion

The effect of NaF and CaO/SiO$_2$ ratio on the hydrogen solubility in the NaF–CaO–SiO$_2$–FeO$_t$ flux system at 1 823 K was studied. At higher NaF content, depolymerization sites occurred, where Si–OH and FeO(OH) bonds from the Raman analysis decrease resulting in lower hydrogen solubility with NaF additions. Higher basicity resulted in a parabolic trend showing a minimum near 1.1 and subsequently increased with further increments in CaO/SiO$_2$. At low basicity the NaF and CaO/SiO$_2$ affected the incorporated hydroxyl system via depolymerization of the flux system. Depolymerization lowers the activity of bridged oxygen ions (O$^-$), consequently free oxygen increased, lowering the hydrogen solubility. At higher basicity, the increase in free oxygen ions results in higher hydrogen solubility. Furthermore it was observed that...
hydrogen could be incorporated into the ferric network as $\delta$-FeO(OH) and $\gamma$-FeO(OH), which increases the quantity of hydrogen in the flux. As the initial FeO redistribute as FeO and Fe$_2$O$_3$, hydrogen can be incorporated with Fe$_2$O$_3$ according to the aforementioned ferric hydroxyls. Higher concentrations of Fe$_2$O$_3$ at CaO/SiO$_2$ of 1.3 showed higher hydrogen solubility due to the increase in incorporated hydroxyl. The amount of FeO(OH) was not significant, but could be detected in the Raman analysis showing a slight decrease with higher basicity.

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