Hydrogen Dissolution in the CaF$_2$–CaO–SiO$_2$ System

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(Received on June 13, 2011; accepted on August 15, 2011)

The hydrogen solubility in the CaF$_2$–CaO–SiO$_2$ slag system has been studied to identify and compare the hydrogen dissolution behavior according to basicity and CaF$_2$ content at high temperature of 1823 K. The hydrogen solubility typically increases with higher CaF$_2$ content across the entire compositional range, but its effect is more pronounced at higher basicity. At low basicity, CaF$_2$ seems to slightly polymerize the slag network increasing the available incorporation sites, where hydrogen can attach and increase hydrogen content in slag. At high basicity, the slag structure is already highly depolymerized and CaF$_2$ addition does not affect the silicate structure, but likely affects the slag hydrogen solubility by lowering the hydroxyl activity. CaO additions lowered the hydrogen content in slag at low basicity and increased the hydrogen content in slag at high basicity. From the temperature dependence of the hydrogen solubility, the dissolution energy of hydrogen in slag was found to be 42.3 kcal/mol.

KEY WORDS: hydrogen solubility; slag structure; FTIR; free hydroxyl; incorporated hydroxyl; basicity.

1. Introduction

With the development of new high strength steels, there has been an increased focus on the control of diffusible hydrogen in weld joints and its impact on materials failure. Excess hydrogen in steel has been known to cause hydrogen induced cracking, embrittlement, and pores in steels. In high strength steels, hydrogen less than 10 ppm can have a serious effect on the physical properties of steel welds. Thus, the control of hydrogen contents to sub ppm levels is essential in achieving the required strength and weld-ability of those steels. To achieve these sub ppm levels, not only is the filler metal important, but also an optimized welding flux (or slag) with a high hydrogen capacity is needed. Industrial welding fluxes designed for high hydrogen capacity is typically CaO based fluxes with SiO$_2$ and halides. However, there has been relatively little work done on the hydrogen dissolution with these welding type fluxes, but some work has been done with steelmaking slags.

According to previous work,$^{2–5)}$ hydrogen solubility can be affected by temperature and slag composition. In particular, the basicity of the slag, where the basicity is defined as the ratio of the basic component over the acidic component, seems to have a profound effect on the mechanism of hydrogen dissolution in slags. Rosenqvist$^6)$ and Ban-ya et al.$^7)$ reported hydrogen dissolves in slags as either an incorporated hydroxyl or a free hydroxyl. In an acidic slag of low basicity, the hydrogen dissolved as an incorporated hydroxyl according to reaction (1). In a basic slag, the hydrogen was assumed to dissolve as a free hydroxyl according to reaction (2).

\[
\text{Incorporated hydroxyl: } H_2O + Si – O – Si \rightarrow 2 Si – OH \quad (1)
\]

\[
\text{Free hydroxyl: } H_2O + O^2– = 2OH^- \quad (2)
\]

Beyond the temperature and slag composition, Ban-ya et al.$^7)$ also found the water solubility in slag to be proportional to the square root of the water vapor pressure ($P_{H_2O}$). The water solubility in slag, which can be defined by the hydroxyl capacity ($C_{OH}$), is represented by Eq. (3).

\[
C_{OH} = \frac{(\text{mass}\% H_2O)(P_{H_2O}/P^o)^{1/2}}{\text{molecular mass of H}_2\text{O}} \quad (3)
\]

where (mass\% $H_2O$), $P_{H_2O}$ (atm) and $P^o$ (atm) are the mass\% $H_2O$ in slag, the partial pressure of $H_2O$ in the gas phase at equilibrium and the atmospheric pressure, respectively. The hydroxyl capacity of a slag allows the direct comparison between different slag compositions. Ban-ya et al.$^7)$ suggested that the hydroxyl capacity decreases with additions of basic oxides such as CaO in an acidic slag system reaching a minimum value at approximately unit basicity in the CaO–SiO$_2$ slag at 1873 K. Iwamoto et al.$^9)$ using gas chromatography observed hydrogen increased with CaF$_2$ additions in the CaO–SiO$_2$ based acidic slag system with $X_{CaO}/X_{SiO_2}$ of less than unity. However, the hydrogen remained constant or
decreased with CaF$_2$ addition in the CaO–SiO$_2$ based basic slag system with X$_{CaO}$/X$_{SiO_2}$ of higher than unity. According to Iwamoto et al.,$^9$ fluorine addition is effective in lowering hydrogen absorption in the fluorosilicate slag as long as the fluorine ions bond with the cation modifier (M) resulting in M–F bonds in the basic slags. Plessis et al.$^{10}$ observed an increase in the hydroxyl capacity for highly basic industrial welding fluxes with lower CaF$_2$ or higher CaO/SiO$_2$ ratio from 2.0 to 3.0.

Thus, the hydrogen solubility is directly related to the composition of the slag, which can dissolve in slag either as an incorporated hydroxyl or free hydroxyl mechanism, and since the composition of the slag directly controls the slag structure, it may be possible to correlate the hydrogen dissolution behavior to the slag structure. According to Ueda et al.$^{11}$ and Park et al.$^{12}$ the depolymerization reaction of the bridged oxygen (O$^\delta$) and the non-bridged oxygen (O$^\gamma$) in the silicate by fluorine ions can be described by the following reactions (4) and (5), respectively.

$$[Si_2O_5]^\delta + 2F^- = [Si_2OF]^\delta + [SiO_2F]^\gamma \quad (4)$$

$$[Si_2O_5F]^\delta + [SiO_2F]^\gamma + 2F^- = [SiO_2F]^\gamma + [SiO_2F]^\gamma + O_2^- \quad (5)$$

As the result of these reactions, the silicate network structure is depolymerized and free oxygen ions (O$^\gamma$) are formed. Kim et al.$^{13}$ using XPS analysis studied the effect of CaF$_2$ additives on the viscosity and slag structure of CaO–SiO$_2$–Na$_2$O based slag system. It was suggested that CaF$_2$ decreases the viscosity by breaking the network structure of molten fluxes and showed the decrease of bridged oxygen in large silicate poly-anions and subsequently increased O$^\gamma$ and O$^\delta$. Hayashi et al.$^{14}$ has also shown that at low basicity, CaF$_2$ additions depolymerize silicate network structure, but at relatively high basicity Ca–F is formed from the additions of CaF$_2$ and the effect on the slag depolymerization is negligible. Unlike the depolymerization observed by Ueda et al.$^{11}$ Park et al.$^{12}$ and Kim et al.$^{13}$, Luth$^{15}$ and Sasaki et al.$^{16,17}$ observed the polymerization of molten CaF$_2$–CaO–SiO$_2$ slags when CaO was substituted with CaF$_2$. The replacement of CaO by CaF$_2$ suggested that a single O ion is replaced by two F ions without changing the total amount of Ca and Si. When two F ions are introduced, a non-bridging oxygen is removed from the silicate tetrahedral, but the fluorine ions do not take the tetrahedral position due to the presence of CaF$^\gamma$ and loosely bonded Ca–F complexes are formed along with a dangling silicon bond. The instability of this dangling silicon bond is likely to incorporate one of the non-bridged oxygens and actually polymerize into a larger silicate. Asada et al.$^{18}$ also studied the slag structure of the molten CaO–CaF$_2$–SiO$_2$ system, where the substitution of CaF$_2$ for CaO enhanced the polymerization of the melt up to 25 mol% of CaF$_2$. Above 25 mol% CaF$_2$, the polymerization was suppressed because F ions substituted the oxygen ion position in the Si–tetrahedral poly-anion which decreases the fraction of Q$^4$+Q$^3$. Mysen and Richet$^{19}$ has also reported the general interaction between F and the aluminosilicate network by using monovalent metal cations, M$^+$.

In peralkaline silicate melts, fluorine bearing compounds can be formed by the following reaction (6), which result in silicate polymerization.

$$2Q_3 + 2M^+ + MF = 2Q_4 + M_2OF \quad (6)$$

where Q$^3$ and Q$^4$ is the silicate structure with NBO/Si=1 and NBO/Si=0, respectively.

In this study, the hydrogen solubility of the CaF$_2$–CaO–SiO$_2$ slag system has been studied in a wide range of composition. The effect of basicity, CaF$_2$ temperature, and CaO on the hydrogen solubility of this slag system was observed and correlated with the slag structure using FTIR (Fourier Transformed Infra-Red) analysis.

2. Experimental

Reagent grade chemicals of CaF$_2$, CaO, and SiO$_2$ were used to prepare the slag samples. The samples were pre-melted at 1 823 K under 200 sccm of Ar gas in a platinum crucible for 5 hours to obtain a homogeneous slag sample. Pre and post experimental chemical composition of the fluxes using the XRF (X4 Explorer, Bruker) is shown in Table 1. As can be seen, significant fluorine vaporization can occur depending upon the chemical composition of the slag system. Thus, the post experimental compositions were taken to be the true compositions for the conditions of the thermal equilibrium technique. This vaporization is likely caused by the fluorine vaporization as SiF$_4$ and HF, the details of which have been provided elsewhere.$^{20}$ Figure 1 shows a schematic of the experimental apparatus. Ar gas of 200 sccm was passed through a column of water at a set temperature. A humidifying vessel set at 333 K can retain an H$_2$O partial pressure of approximately 0.2 atm (152 mm-Hg). The gas inlet line after the humidifying vessel was electrically heated at 353 K. This wet Ar gas was injected into the hot zone of a Kanthal vertical resistance furnace. The temperature of the furnace was calibrated using a reference B-type thermocouple and controlled within ± 3 K using a PID controller. The slag sample was then equilibrated for 5 hrs at 1 823 K to ensure that a thermodynamic equilibrium was reached for the hydrogen dissolution into molten slag. After equilibration, the slag sample was removed from the hot zone of the furnace and quenched by a water-cooled copper mold. The as-quenched sample was kept within an Ar gas purged container for not more than 48 hours and the hydrogen was analyzed using a LECO RH-600 inert gas fusion technique with thermal conductivity detection. Verification and reproducibility of the hydrogen analysis has been provided in a previously published paper.$^{20}$

3. Results and Discussion

3.1. Effect of CaF$_2$ on Hydrogen Solubility and Slag Structure at Fixed Basicity

Figure 2 shows the hydrogen solubility as a function of the CaF$_2$ mole fraction (X$_{CaF_2}$) at fixed basicities (X$_{CaO}$/X$_{SiO_2}$). In general, the hydrogen solubility increases with higher CaF$_2$ content, but CaF$_2$ significantly increases the hydrogen solubility for slag compositions at higher basicity. In particular, at X$_{CaO}$/X$_{SiO_2}$ of 2.6, the hydrogen solubility increases from approximately 50 ppm to 230 ppm as the X$_{CaF_2}$ is increased from 0.14 to 0.33. This sudden increase in the hydrogen content and also the apparent discrepancy...
at higher basicity with Plessis et al.\textsuperscript{10} has yet to be fully understood, but if we assume the free hydroxyl mechanism expressed in reaction (2) to be prevalent at this high basicity, CaF\(_2\) can either depolymerize the bridged oxygen bonds of the complex silicate structures increasing O\textsuperscript{2–} and the activity of O\textsuperscript{2–} (\(a_{O^{2–}}\)) or lower the activity of the free hydroxyl (\(a_{OH^{–}}\)). Much work regarding the depolymerization effect of CaF\(_2\) at low basicity of CaO/SiO\(_2\) less than unity have already been done in previous works\textsuperscript{12–14,21–24} and a detailed review is beyond the scope of this paper, but there seems to be a consensus, that at high basicity or low SiO\(_2\) activity, fluorine ions are associated with Ca ions suggesting CaF\(_2\) does not modify the silicate structure nor participate in the

| No. | Composition | H (mass ppm) | P\(_{H_2O}\) (atm) | Temperature (K) |
|-----|-------------|---------------|---------------------|-----------------|
|     | CaF\(_2\) (mol%) | SiO\(_2\) (mol%) | CaO (mol%) | CaF\(_2\) (mol%) | SiO\(_2\) (mol%) | CaO (mol%) | AVG | STDEV |
| FCS1 | 7.57 | 33.03 | 59.4 | 4.83 | 31.23 | 63.94 | 14.63 | 1.89 | 1823 |
| FCS2 | 11.55 | 31.59 | 56.91 | 8.75 | 30.59 | 60.66 | 17.81 | 1.14 | 1823 |
| FCS3 | 15.55 | 30.11 | 54.34 | 12.42 | 28.92 | 58.66 | 20.32 | 1.4 | 1823 |
| FCS4 | 32.93 | 23.97 | 43.1 | 31.23 | 22.92 | 45.85 | 35.23 | 3.66 | 1823 |
| FCS5 | 52.49 | 16.94 | 30.57 | 50.89 | 16.14 | 32.97 | 59.23 | 5.94 | 1823 |
| FCS6 | 33.48 | 47.64 | 18.88 | 17.97 | 42.76 | 39.27 | 15.72 | 1.42 | 1823 |
| FCS7 | 33.15 | 33.39 | 33.46 | 27.85 | 31.27 | 40.88 | 22.62 | 1.15 | 1823 |
| FCS8 | 7.66 | 51.29 | 41.05 | 3.75 | 45.3 | 50.95 | 6.72 | 1.17 | 1823 |
| FCS9 | 15.73 | 46.82 | 37.45 | 9.5 | 43.7 | 46.8 | 10.35 | 0.87 | 1823 |
| FCS10 | 33.24 | 37.09 | 29.67 | 26.54 | 34.19 | 39.27 | 18.54 | 2.87 | 1823 |
| FCS11 | 52.83 | 26.2 | 20.97 | 49.39 | 23.97 | 26.64 | 20.25 | 1.61 | 1823 |
| FCS12 | 15.49 | 24.15 | 60.36 | 14.06 | 23.56 | 62.38 | 59.13 | 9.19 | 1823 |
| FCS13 | 23.9 | 21.74 | 54.36 | 22.92 | 21.3 | 55.78 | 91.43 | 3.78 | 1823 |
| FCS14 | 32.82 | 19.19 | 47.99 | 31.16 | 18.9 | 49.94 | 232.67 | 19.3 | 1823 |
| FCS15 | 15.45 | 19.14 | 63.41 | 13.93 | 20.48 | 65.59 | 150.67 | 12.7 | 1823 |
| FCS16 | 32.77 | 16.81 | 50.42 | 31.28 | 16.27 | 52.45 | 23.27 | 23.01 | 1823 |
| FCS17 | 32.87 | 21.36 | 45.77 | 30.99 | 21.07 | 47.94 | 68.16 | 4.1 | 1723 |
| FCS18 | 32.87 | 21.36 | 45.77 | 31.37 | 21.05 | 47.58 | 104.17 | 13.18 | 1823 |
| FCS19 | 32.87 | 21.36 | 45.77 | 30.95 | 21.06 | 47.99 | 128 | 12.49 | 1923 |
| FCS20 | 39.29 | 33.73 | 26.98 | 31.41 | 32.42 | 36.17 | 25.73 | 3.44 | 1823 |
| FCS21 | 33.59 | 52.38 | 14.03 | 33.78 | 31.41 | 34.81 | 25.07 | 3.56 | 1823 |
Depolymerization of the molten slag structure. If depolymerization does not occur, the addition of CaF$_2$ is not likely to affect O$^{2-}$. Therefore in basic slags where hydrogen dissolves as free hydroxyl (OH$^-$) and free oxygen activity (aO$_2^-$) is unaffected, the addition of CaF$_2$ at constant X$_{CaO}$/X$_{SiO_2}$ is likely to increase the absolute Ca$^{2+}$ concentration in the slag and lower the activity of the hydroxyl ion (aOH$^-$) subsequently pushing reaction (2) to the right and increasing the hydrogen solubility.

In order to correlate the hydrogen solubility with the slag structure and also identify the dissolution mechanism of hydrogen according to the slag composition, FTIR analysis of as-quenched slag samples were done. Figure 3 shows the FTIR transmittance trough as a function of wavenumber (cm$^{-1}$) for different CaF$_2$ contents and a fixed X$_{CaO}$/X$_{SiO_2}$ of 1.0. The transmittance trough for Si–OH, which corresponds to the deformation vibration of the incorporated hydroxyl, is observed at about 850 cm$^{-1}$.[25] Also, a weak [SiO$_4$]-tetrahedral symmetric stretching band for NBO/Si=1 corresponding to the large silicate sheet structure is observed near 1060 cm$^{-1}$. At X$_{CaO}$/X$_{SiO_2}$ of 1.0, the hydrogen solubility increases while the Si–OH transmittance trough and the symmetric stretching bands for NBO/Si=1 become more pronounced with higher CaF$_2$. Although weak, a more pronounced NBO/Si=1 stretching band typically suggests a stronger slag network structure. And a more pronounced transmission trough of the Si–OH deformation vibrations with higher hydrogen solubility suggest the incorporated hydroxyl mechanism described by reaction (1) is dominant for the slag composition. If the incorporated hydroxyl as described in reaction (1) is valid and dominant at X$_{CaO}$/X$_{SiO_2}$ of 1.0 and the addition of CaF$_2$ increases the hydrogen solubility, CaF$_2$ seems to be increasing the activity of the bridged oxygen within the Si–O–Si bonding as expressed in reaction (1). In order to increase the activity of the bridged oxygen, the silicate structure needs to be polymerized with CaF$_2$ additions. Therefore, considering the pronounced Si–OH deformation vibration trough and NBO/Si=1 stretching band, the addition of CaF$_2$ seems to have slightly polymerized the slag network. The bands near 680 cm$^{-1}$ have been suggested by Luth[15] and Nakamoto[26] to be the [SiF$_6$]$^{2-}$-octahedral complexes, but has yet to be fully verified. No physical correlations could be ascertained from this speculated weak transmittance peak.

Polymerization of silicate slags with CaF$_2$ additions is not typical and a direct polymerization model has yet to be fully developed. According to Sasaki et al.[16,17] and Luth[15] at certain slag compositions when CaF$_2$ substitutes CaO in calcium-silicate slags, F ions tends to bond with Ca ions and form loosely bonded Ca–F complexes and the formation of such complexes can inhibit the typical depolymerization role of CaF$_2$ in slags. Work done by Zimova and Webb[27] showed an increase of viscosity with Cl addition in the Na$_2$O–Fe$_2$O$_3$–Al$_2$O$_3$–SiO$_2$ at certain compositions and indicated a polymerization of the melt with certain halide compound additions. Mysen et al.[28] showed similar results of polymerization with fluorine additions to the meta-alumino-silicate glasses, where polymerization of the silicate network could occur by reactions previously described in reaction (6) and provided a simple reaction mechanism for polymerization when NaF is added to the Na$_2$O–SiO$_2$ slag system, which is described in reaction (7).

$$2Q^3 + Na^+ + NaF = 2Q^4 + Na_3OF.$$

The above results of Mysen et al.,[28] although not exact, seem to be approximately at fixed basicity with comparison between fluorine containing and fluorine free slags. Thus, the increase in hydrogen content and the pronounced increase in the Si–OH bending troughs with higher CaF$_2$ content at X$_{CaO}$/X$_{SiO_2}$ of 1.0 seem to suggest a weak polymerization effect of CaF$_2$ and the subsequent increase in slag hydrogen content to be related to the incorporated hydroxyl mechanism. However, the Ca–F bond is highly ionic at about 80% based on Pauling’s electronegativity concept resulting in lower FTIR transmission bands for the stretching vibrations involving these complexes and is not observed in the present FTIR spectra.[12,15]

Figure 4 shows the FTIR transmittance trough as a function of the wavenumber (cm$^{-1}$) with different CaF$_2$ contents and X$_{CaO}$/X$_{SiO_2}$ of 2.6. For highly basic slags, the network structure is comparatively more modified than for a low basicity slag, which has been explained in various publica-

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**Fig. 3.** FTIR analysis of the as-quenched CaF$_2$–CaO–SiO$_2$ slag samples at X$_{CaO}$/X$_{SiO_2}$ of 1.0 and various CaF$_2$ content.**

**Fig. 4.** FTIR analysis of the as-quenched CaF$_2$–CaO–SiO$_2$ slag samples at X$_{CaO}$/X$_{SiO_2}$ of 2.6 and various CaF$_2$ content.
In particular, since the hydrogen dissolution in basic slags follows the free hydroxyl mechanism expressed by reaction (2), increased activity of free oxygen ions \((a_{O^2-})\) or a decrease in the activity of hydroxyl \((a_{OH^-})\) should result in higher slag hydrogen content. With CaF\(_2\) additions, the hydrogen solubility significantly increases, but the Si–OH deformation trough for the mechanism of incorporated hydroxyl is unchanged. Furthermore, appreciable changes in the NBO/Si=1 stretching band is not observed. This seems to indicate that the hydrogen dissolution mechanism in the highly basic slag is likely in the form of a free hydroxyl \((OH^-)\) as described by reaction (2) and that the addition of CaF\(_2\) does not significantly affect the slag network structure. However, the hydrogen solubility was seen to increase rapidly. Since CaF\(_2\) does not participate in significant depolymerization of the slag and additional free oxygen ions \((O^2-)\) are not supplied to the slag system, the increase in the hydrogen solubility with CaF\(_2\) additions at \(X_{CaO}/X_{SiO_2}\) of 2.6 is likely a result of the excess Ca\(^{2+}\) ions provided by CaF\(_2\) and the subsequent decrease in the activity of hydroxyl \((a_{OH^-})\). It should also be noted that the approximate melting temperature calculated by Fact-Sage\(^8\) for the various slag samples provided in Figs. 3 and 4 were significantly different. Slag samples with large hydrogen solubilities of more than 90 ppm had significantly lower melting temperatures, which were close to the eutectic composition of the CaF\(_2\)–CaO–SiO\(_2\) slag system.

3.2. Effect of Basicity on Hydrogen Solubility and Slag Structure at Fixed CaF\(_2\)

Figure 5 shows the hydrogen solubility in the CaF\(_2\)–CaO–SiO\(_2\) slag system as a function of the perceived basicity or the molar Vee ratio \((X_{CaO}/X_{SiO_2})\) at fixed CaF\(_2\) mole fraction of 0.13 and 0.31. The hydrogen solubility is relatively unchanged for \(X_{CaO}/X_{SiO_2}\) of less than 2.0, but rapidly increases with higher basicity above \(X_{CaO}/X_{SiO_2}\) of 2.0. In addition comparison of the hydrogen solubility for \(X_{CaF_2}\) of 0.13 and 0.31 at low basicity shows the effect of CaF\(_2\) to be minimal compared to the effect of CaF\(_2\) on the hydrogen solubility at high basicity. Thus, the polymerization effect of CaF\(_2\) if any at \(X_{CaO}/X_{SiO_2}\) of less than 2.0 and the incorporated hydroxyl is likely to be small. At higher basicities, the aforementioned Ca\(^{2+}\) effect on the free hydroxyl and the melting temperature seems to be important in increasing the hydrogen content. Figure 6 shows the FTIR analysis of slags at relatively wide range of basicity from 1.0 to 3.2 and a fixed CaF\(_2\) mole fraction of 0.31. As expected with higher basicity, the hydrogen solubility increases, but no significant differences among the highly basic samples can be observed in the FTIR analysis for the wavenumbers between 4 000 cm\(^{-1}\) to 400 cm\(^{-1}\). The weak Si–OH bending vibration band between 870–820 cm\(^{-1}\) is observed, but become less pronounced as the basicity is increased, which is expected when the free hydroxyl mechanism is dominant. Similar result were observed for \(X_{CaF_2}=0.13\) at various basicities.

3.3. Effect of CaO at Fixed SiO\(_2\) Content

Figure 7 shows the hydrogen solubility as a function of the \(X_{CaO}\) at fixed SiO\(_2\) content of 0.16 and 0.24. The hydrogen solubility increases with higher CaO content in both cases. The addition of CaO increased the free oxygens and promotes the formation of free hydroxyl as shown from
reaction (2). The hydrogen solubility was found to increase significantly in the highly basic slags with higher $X_{\text{CaO}}$.

**Figure 8** shows the hydrogen solubility as a function of $X_{\text{CaO}}$ at fixed SiO$_2$ content of 0.31 and 0.44. At relatively high SiO$_2$ content and acidic slag composition, the addition of CaO lowers the hydrogen solubility due to the supply of free oxygen ions from excess CaO, which can break the bridged oxygen bond, lowering the number of hydroxyl incorporation sites and subsequently lowering the solubility.$^{3,4,9,29–31}$

**Figures 9** and **10** show the FTIR analysis as a function of wavenumber (cm$^{-1}$) with various $X_{\text{CaO}}$ at fixed SiO$_2$ content of 0.24 and 0.31, respectively. At a fixed $X_{\text{SiO}_2}$ of 0.24, a weak $[\text{SiO}_4]$-tetrahedral stretching bands for NBO/Si of 1 near 1 060 cm$^{-1}$ (NBO/Si=1 units) is observed for $X_{\text{CaO}}$ of 0.28 and disappears from $X_{\text{CaO}}$ of 0.46 and higher. The Si–OH bending trough also becomes less pronounced with increased $X_{\text{CaO}}$, which suggests that in this slag system, the dissolution behavior of hydrogen changes from the incorporated hydroxyl to the free hydroxyl mechanism with increased $X_{\text{CaO}}$. The weak $[\text{SiF}_6]^{2-}$-octahedral stretching vibration is observed at high concentrations of $X_{\text{CaF}_2}$, but disappeared as $X_{\text{CaF}_2}$ decreases. At a fixed $X_{\text{SiO}_2}$ of 0.31 in Fig. 10, the NBO/Si=1 peak at about 1 060 cm$^{-1}$ is unchanged as the CaO content decreases, but is more pronounced than the transmittance trough observed for $X_{\text{SiO}_2}$ of 0.24 in Fig. 9. Furthermore, as the hydrogen solubility increases with lower CaO content, the Si–OH peak becomes slightly pronounced suggesting the incorporated hydroxyl becomes more important as the slag composition becomes more acidic.

3.4. Effect of Temperature on Hydrogen Dissolution in Molten Slags

At constant $P_{\text{H}_2\text{O}}$ of 0.2 atm, the hydrogen content in the CaF$_2$–48 mol% CaO–21 mol% SiO$_2$ as a function of temperature from 1 723 to 1 923 K is shown in **Fig. 11**. As expected, the hydrogen solubility increases with higher temperatures. In order to obtain the heat of hydrogen dissolution in slag, the Van’t Hoff equation derived from the Gibbs-Helmholtz relationship at constant pressure and the thermodynamic equilibrium constant is typically used. For thermo-
dynamic equilibrium of hydrogen dissolution in slag using water vapor, the equilibrium constant is the hydrogen content of the slag at the temperature of interest and is expressed in Eq. (8).

\[ L = 2R \ln[H_2 - H_1]/(1/T_1 - 1/T_2) \] ........................ (8)

where \( L \), \( R \) and \( H_{1,2} \) is the heat of hydrogen dissolution in slag and the gas constant and the hydrogen contents at temperature, \( T_{1,2} \), respectively. From the slopes of the natural logarithm of mass ppm H as a function of reciprocal temperature \((1/T)\), \( L \) was obtained.

The dissolution energy of hydrogen was calculated to be is 42.3 kcal/mol. According to Imai et al.\(^{14}\) in the CaO–40.6 mol% SiO\(_2\)–32.8 mol% FeO slags system and P(H\(_2\)O) of 0.1 atm, the energy of hydrogen dissolution was 13 kcal/mol.

4. Conclusion

The hydrogen solubility in the CaF\(_2\)–CaO–SiO\(_2\) slag system at 1823 K has been studied. The hydrogen solubility typically increases with higher CaF\(_2\) content, but its effect on hydrogen solubility is more pronounced at higher basicity. CaF\(_2\) seems to have a different behavior according to the basicity of the slag. At low basicity of about \( X_{\text{CaO}}/X_{\text{SiO}}=1.0 \), CaF\(_2\) additions slightly polymerizes the slag structure and increases the number of available incorporation sites. In contrast, at high basicity of about \( X_{\text{CaO}}/X_{\text{SiO}}=2.6 \), the slag structure is already highly depolymerized and CaF\(_2\) addition does not affect the silicate structure, but likely affects the slag hydrogen solubility by lowering the hydroxyl activity \((a_{\text{OH}}^-)\) with excess Ca\(^{2+}\). In general, the effect of CaO on the hydrogen solubility and slag structure is stronger than CaF\(_2\). From the temperature dependence, the energy of hydrogen dissolution was calculated to be 42.3 kcal/mol in a highly basic slag system with CaF\(_2\) of 0.31.

Acknowledgements

This study was partially supported by the Brain Korea 21 (BK21) Project at the Division of the Humantronics Information Materials and the Ministry of Knowledge Education Project No. 2010-8-1523.

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