Hydrogen Control in Steel Weld Metal by Means of Fluoride Additions in Welding Flux

Experiments proved the effectiveness of fluoride additions in reducing hydrogen in weld metal

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ABSTRACT. Development of high-strength steels in recent years has required the weld metal to also improve in terms of mechanical properties. However, strengthening the weld metal tends to increase susceptibility to hydrogen-assisted cracking (HAC); therefore, diffusible hydrogen content in the weld metal, attributed to be a major cause of HAC, must be drastically reduced. Flux ingredients containing fluoride ions (F^{-1}) such as fluorspar (CaF_2) have been reported to reduce diffusible hydrogen content in steel welds. It is believed fluoride reacts with hydrogen in the arc atmosphere to form HF, which is removed from the molten iron because of its low solubility.

Preliminary thermodynamic calculations considering the reaction between hydrogen in the arc atmosphere and the fluoride in the slag were performed and predict that KF, MnF_3 and K_3AlF_6 are more effective in reducing hydrogen than CaF_2, which is a common flux ingredient. To verify their predicted effectiveness, experimental FCAW consumables with additions of these fluorides were designed and fabricated at the Colorado School of Mines (CSM). Welds were produced using these electrodes and the amounts of diffusible hydrogen were measured. The experiments proved the effectiveness of fluoride additions as predicted by the thermodynamic calculations. For example, reductions of 39–67%, 21–34% and 22–31% in diffusible hydrogen were achieved with the additions of 7.4 wt-% of KF, 4.8 wt-% of MnF_3 and 5.5 weight percent of K_3AlF_6, respectively, in comparison with the experimental results with those of the base electrode (with only CaF_2).

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Introduction

Development of High-Strength, Low-Alloyed (HSLA) Steels

For the welding of high-strength structural steels, the achievement of high weldability (lower susceptibility for hydrogen-assisted cracking [HAC]), together with performance requirement has been the most important issue. The strength of quench and temper (QT) steel is based on high hardenability, *i.e.*, high carbon and alloying contents. Therefore, low-temperature products such as bainite and martensite tend to appear in the heat-affected zone (HAZ) after welding. These products exhibit high dislocation density, which elevates the internal stress in the HAZ. Since HAC tends to occur in the stress-concentrated areas in the presence of hydrogen, it is highly likely HAC occurs in the HAZ of welded joints of QT steels. To avoid HAC, preheating or postheating is performed, as seen in shipbuilding practices. However, for cost savings, it would be preferred these processes be eliminated or simplified. To satisfy these requirements, research and development programs of structural steels have been directed toward their weldability and mechanical properties.

KEY WORDS
Hydrogen-Assisted Cracking
High-Strength Low-Alloy Steels
Gas Metal Arc Welding
Flux Cored Welding Wires
Diffusible Hydrogen

The high-strength, low-alloyed (HSLA) steels were developed by minimizing the impurities and alloying element contents. The HSLA-80 and HSLA-100 steels developed by the U.S. Navy during the 1980s contain very low carbon (0.04%) and sulfur (0.005%) contents, and a certain amount of copper addition (1.20 – 1.60%) (Ref. 1). Since carbon is the most influential element on the HAC susceptibility, the low carbon contents of the HSLA steels make them very weldable, although their carbon equivalent values (CEV) may be as high as those of the QT steels. On the other hand, the mechanical properties of the HSLA steel welds are as excellent as the QT steels. This enhancement is mainly obtained by copper precipitation strengthening because of higher additions of copper in these HSLA steels. These steels are also processed by thermomechanical-controlled processing (TMCP), which includes controlled (low finishing temperature) rolling, accelerated cooling from the rolling temperature and direct quenching after rolling. These technologies have also provided excellent performance to high-strength steels.

Development of Welding Materials for High-Strength Steels

Regarding the welding materials for high-strength steels, the mechanical properties of weld metals must match those of the base materials and meet sets of preestablished specifications. Thus, the reduction of weld metal diffusible hydrogen content becomes the major issue. The reported improvement of weld metal strengths was achieved by optimizing the CEV; therefore, as the strength in weld metals increases, a higher HAC susceptibility may result. The upper limit of acceptable weld metal diffusible hydrogen content for high-strength steel welding

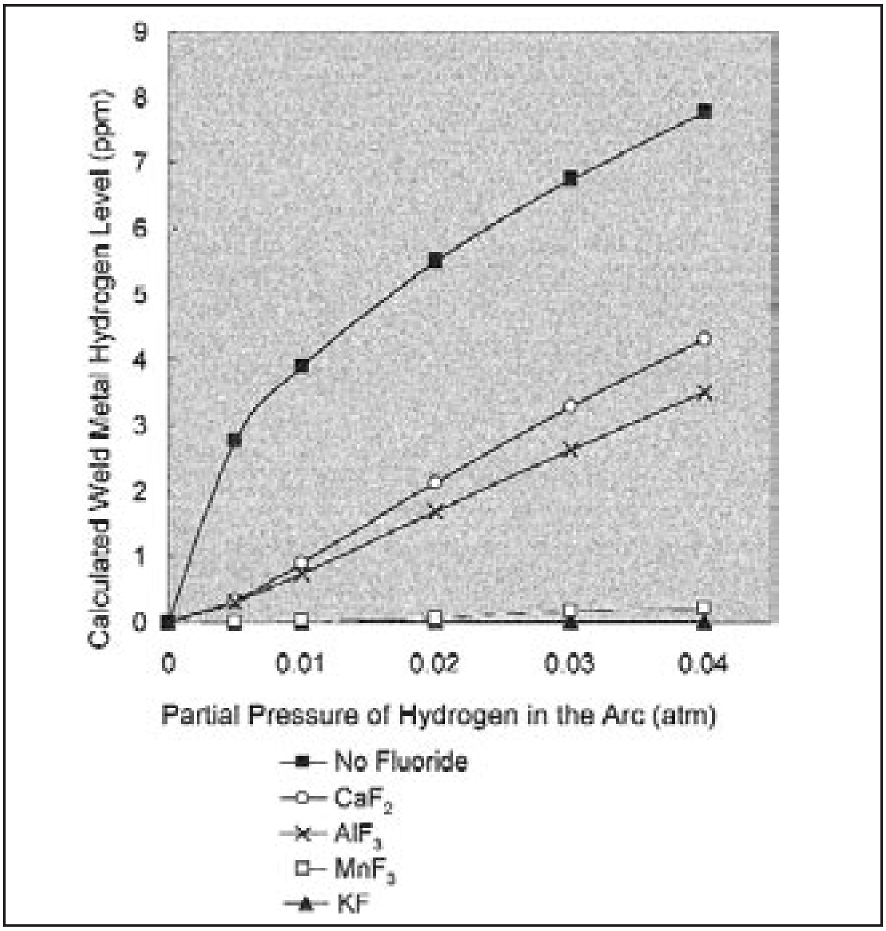

Fig. 1 — Calculated hydrogen content in liquid iron at 2050°C as a function of partial pressure of hydrogen under the presence of an equal amount of fluorine associated with the respective fluorides.

has been set at 5 mL/100 g of deposited metal. However, more recent development of high-performance steels with "enhanced" mechanical properties requires the diffusible hydrogen level be lowered to 1 mL/100 g of deposited metal. Much research and development work has been directed toward minimizing the diffusible hydrogen in the weld, as discussed in the next section.

Methods of Minimizing Diffusible Hydrogen in the Weld Metal

Modifying Flux Ingredients

Terashima, *et al.* (Ref. 2), and Surian, *et al.* (Ref. 3), investigated the effect of basicity of the welding slags on the diffusible hydrogen in the weld metal. Terashima, *et al.*, defined the hydrogen behavior in submerged arc welding with agglomerated CaO-SiO_2-FeO-type fluxes. They changed slag basicity indicated as B_L in Equation 1, from -1.5 to 3.07 by changing SiO_2 additions from 55.5 to 18.5%. and CaO additions from 18.4 to 55.4%. They found the diffusible hydrogen level decreased from 12 to 2 mL/100 g when B_L increased from 0 to 3.

$$B_L^{*} = 6.05N_{CaO} - 6.35N_{SiO_2} - 4.97N_{TiO_2} - 0.2N_{Al_2O_3} + 4.8N_{MnO} + 4.0N_{MgO} + 3.4N_{FeO} \quad \text{(N: mole fraction)} \tag{1}$$

Surian, *et al.* (Ref. 3), reported the same effect of increasing slag basicity on the reduction of diffusible hydrogen. They replaced silica with wollastonite (calcium silicate, 50%CaO/50%SiO_2) in the covering of E6013 rutile steel electrodes for shielded metal arc welding. In their experiments, basicity index, as defined by Tuliani, *et al.* (Ref. 4), as shown in Equation 2, was increased from 0.31 to 0.51 by reducing silica from 16 to 0% while increasing calcium silicate from 0 to 16%.

$$BI = \frac{Cao + MgO = BaO + SrO}{SiO_2} + \frac{Na_2O + Li_2O + CaF_2 + \frac{1}{2}(MnO + FeO)}{\frac{1}{2}(Al_2O_3 + TiO_2 + ZrO_2)} \quad \text{(comp. in wt\%)} \tag{2}$$

This adjustment of slag basicity resulted in the decrease of diffusible hydrogen from 41.1 to 23.5 mL/100 g.

Controlling Oxygen Content in the Weld Metal

The effect of oxygen on diffusible hydrogen has been investigated by several researchers (Refs. 5–9) with the objective of establishing a better understanding of the relationship between oxidizing electrodes and diffusible hydrogen. It is shown oxidizing electrodes are able to deposit welds with lower hydrogen content but also with higher oxygen content, when compared with rutile electrodes (Ref. 10). This effect can be attributed to the following equilibrium reaction;

$$H_2O_{(g)} \Leftrightarrow 2\underline{H} + \underline{O} \tag{3}$$

Based on the law of mass reaction, if the oxygen level (on the right side of equation) is increased, the reaction will be forced to proceed to the left to result in a decrease of the hydrogen level in the system. Accordingly, the diffusible hydrogen level can be controlled by adjusting the oxygen level in weld metal.

Diluting Hydrogen in the Arc with Inert Gas

Weld metal diffusible hydrogen content is generally observed to linearly increase with the square root of the potential pressure of hydrogen in the atmosphere, according to Sievert's law (Refs. 11,12). This relationship exists because moisture in the atmosphere goes into the arc and the hydrogen originated from the dissociation of water may find its way to the weld pool. Several methods have been established to decrease the partial pressure of hydrogen. For example, shielding gases may dilute the hydrogen in the arc plasma and reduce the partial pressure of hydrogen. For shielded metal arc welding or self-shielded flux cored arc welding, calcium carbonate ($CaCO_3$) is often added to the fluxes to reduce the partial pressure of hydrogen. Calcium carbonate decomposes in the arc and generates CO_2, as shown in Equation 4, which reduces the concentration of hydrogen

$$CaCO_3 \rightarrow CaO + CO_2 \tag{4}$$

Reacting Hydrogen with Some Elements to Produce Chemicals Insoluble in Iron

Another method of reducing the partial pressure of hydrogen consists of adding ingredients, such as fluorides, in

Table 1 — Change of Numbers of Mole and Molar Fractions of the Components in the Reaction Between CaF_2 and H_2

Number of Mole	CaF_2 (N_{CaF_2})	H_2 (N_{H_2})	Ca (N_{Ca})	HF (N_{HF})
Initial State	0.1a	0.01b	0	0
Equilibrium State	0.1a-x	0.01b-x	x	2x
Molar Fraction	CaF_2 (X_{CaF_2})	H_2 (X_{H_2})	Ca (X_{Ca})	HF (X_{HF})
Initial State	0.1	0.01	0	0
Equilibrium State	(0.1a-x)/a	(0.01b-x)(b + x)	x/a	2x/(b = x)

Table 2 — Flux Formula of Experimental Electrodes

	Base	5% K_3AlF_6	7.5% K_3AlF_6	10% K_3AlF_6	5%KF	5%MnF_3
Addition of Fluorides	0	5.5	8.3	11	7.4	4.8
CaF_2	20.5	15.5	13.0	10.5	15.5	15.5
Fe	56	55.5	55.2	55.0	53.6	56.2
$CaCO_3$	5.7	5.7	5.7	5.7	5.7	5.7
Al_2CO_3	1.0	1.0	1.0	1.0	1.0	1.0
SiO_2	7.5	7.5	7.5	7.5	7.5	7.5
K_2O	1.0	1.0	1.0	1.0	1.0	1.0
Mn	7.2	7.2	7.2	7.2	7.2	7.2
C	1.1	1.1	1.1	1.1	1.1	1.1

(weight percent)

the flux coating to react with hydrogen and form hydrogen-containing products that are insoluble in liquid iron. For example, CaF_2 (fluorspar) is commercially added to the fluxes of low-hydrogen electrodes. It is believed a part of the CaF_2 dissociates at high temperatures to produce fluorine and the increase of fluorine shifts the reaction in Equation 5 to the right, resulting in reduced hydrogen in the arc.

$$F_2 + H_2 \rightarrow 2HF \tag{5}$$

However, it is also recognized the decomposition of CaF_2 is not particularly active, so most of the CaF_2 remains in the slag. Therefore, researchers have been searching for other fluorides more efficient in weld metal hydrogen reduction. Tsuboi, *et al.* (Refs. 13–16), investigated fluorides more effective in reducing weld metal diffusible hydrogen than CaF_2. They observed greater reduction of diffusible hydrogen with the addition of Na_3AlF_6 to the welding flux. At 8% fluoride additions, the diffusible hydrogen level was 4 mL/100 g of the deposited metal and 30% lower than obtained using CaF_2.

Pokhodnya, *et al.* (Ref. 17), also reported the effectiveness of complex fluorides such as Na_2SiF_6, Na_2TiF_6, K_2SiF_6 and K_2TiF_6. Their experiments were performed with flux cored arc welding (FCAW). To make the fluorine additions constant, the additions of fluorides in weight percent were varied. It is clear from their results complex fluorides give lower diffusible hydrogen levels (between 3.5 and 6.5 mL/100 g) than other fluorides, including CaF_2 (between 5.5 and 10 mL/100 g).

Johnson, *et al.* (Ref. 18), reported the effectiveness of MnF_3 in reducing the diffusible hydrogen level in the weld metal conducted on the primer-coated steel plates. In their experimental results, the hydrogen level was around 70 mL/100 g because of the presence of an epoxy-based organic primer coating of 4.5 mils (0.11 mm) thickness in the absence of fluorides in the welding system. However, with the addition of MnF_3, the diffusible hydrogen content was lowered to 13–15 mL/100 g even with the thick primer coating.

The results of fluoride additions showed they are very effective in minimizing hydrogen pickup in the weld metal. However, the research and development programs reported have not been systematic to include a broader selection of fluorides. Therefore, the investigation of several other fluorides was carried out in this work. First, the candidate fluorides were selected by thermodynamic calculations and then the effectiveness of these fluorides was experimentally verified.

Thermodynamic Prediction

In this section, the thermodynamic model to predict the reduction of diffusible hydrogen by the addition of fluorides will be discussed. To model the reactions that occur in the welding arc and slag during welding, several conditions below are assumed:

- Reactions occur fast at a rate sufficient to reach equilibrium.
- The liquids and gases in the system are ideal solutions so the activities of elements in the reactions can be expressed as their atomic fractions in the liquid or gas.
- The arc is a closed system so there is no exchange of element between outer atmosphere and arc during the reaction.

Assuming these conditions, the calculation was developed for the additions of four fluorides, CaF_2, AlF_3, MnF_3 and KF. The methodology of the calculation will be introduced in the next section using CaF_2 as an example. The calculations for the other fluoride additions are not included because of the similarity to the case of CaF_2.

Calculation of the Changes of the Partial Pressure of Hydrogen by the Reaction of Fluorides with Hydrogen in the Arc Atmosphere

In the presence of CaF_2, the following reaction is assumed to occur on the surface of the slag:

$$CaF_{2(slag)} + H_{2(gas)} = Ca_{(slag)} + 2HF_{(gas)} \tag{6}$$

The reaction in Equation 6 can be assumed to be the combined reaction of the decomposition of CaF_2 (Equation 7) and the generation of HF (Equation 8).

$$CaF_2 = Ca + F_2 \tag{7}$$

$$\tfrac{1}{2}H_2 + \tfrac{1}{2}F_2 = HF \tag{8}$$

The molar free energies (G) of the decomposition of CaF_2 (Equation 7) and the generation of HF (Equation 8) are expressed as Equations 9 and 10.

$$\Delta G_{CaF_2} = \Delta G^o_{CaF_2} + RT1nK_{CaF_2} \tag{9}$$

$$\Delta G_{HF} = \Delta G^o_{HF} + RT1nK_{HF} \tag{10}$$

G° is the standard free energy of the reaction and K is the equilibrium constant and can be expressed as follows:

$$K_{CaF_2} = \frac{a_{Ca} a_{F_2}}{a_{CaF_2}} \tag{11}$$

$$K_{HF} = \frac{a_{HF}}{a_{H_2}^{1/2} a_{F_2}^{1/2}} \tag{12}$$

At equilibrium, G = 0, Equations 9 and 10 become:

$$\Delta G^o_{CaF_2} = -RT1nK_{CaF_2} \tag{13}$$

$$\Delta G^o_{HF} = -RT1nK_{HF} \tag{14}$$

The free energy equation for the reaction in Equation 6 can be given by combining the free energy equation of the decomposition of CaF_2 (Equation 13) and the generation of HF (Equation 14) as expressed in Equation 15.

Fig. 2 — Photograph of the tubular-wire-making facility.

Fig. 3 — Eudiometer tubes and assembly for standard mercury displacement procedure.

Table 3 — Welding Conditions for all the Experiments

Type of Welding Process	Automatic FCAW
Voltage (volts)	29~31
Current (amperes)	260~280
Speed (mm/s)	5.4~6.0
Heat Input (kJ/mm)	1.4
Wire Feed Rate (mm/s)	91.7~104.2
Electrode Extension (mm)	20
Wire Diameter (mm)	1.6

$$\Delta G^\circ_{CaF_2} + 2\Delta G^\circ_{HF} = -RT\ln K_{CaF_2} - 2RT\ln K_{HF} = -RT\ln K_{CaF_2}K_{HF}^2 \quad (15)$$

As mentioned before, K consists of the activities of the elements in reaction. Solving Equation 15 by K results in Equation 16.

$$K_{CaF_2}K_{HF}^2 = \frac{a_{Ca}a_{HF}^2}{a_{CaF_2}a_{H_2}} = \exp\left[-\frac{\Delta G^\circ_{CaF_2} + 2\Delta G^\circ_{HF}}{RT}\right] \quad (16)$$

Assuming the slag and gas are ideal solutions, the activities of the components can be the molar fractions in the slag or in the atmosphere, Equation 16 is expressed as Equation 17

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$$\frac{X_{Ca}X_{HF}^2}{X_{CaF_2}X_{H_2}} = \exp\left[-\frac{\Delta G^\circ_{CaF_2} + 2\Delta G^\circ_{HF}}{RT}\right] \quad (17)$$

If the atomic percent of CaF_2 in the slag is 10% and the partial pressure of H_2 in the arc atmosphere is 0.01 at.-%, the numbers of moles of CaF_2 in the slag and H_2 in the arc atmosphere are given as 0.1a and 0.01b. a and b are the variables that determine the numbers of moles of the slag and gas in the system where the reaction takes place, respectively. Therefore, the numbers of moles of the other ingredients in the slag and the other gases in the system are given as 0.9a and 0.99b. The reaction is assumed to occur in a closed system, and that there are initially 0.1a mole of CaF_2 in the slag and 0.01b mole of H_2 in the arc atmosphere. Neither calcium nor HF exists at this point. Through the reaction in Equation 6, calcium and HF will be produced and the reaction finally reaches equilibrium. At equilibrium, if x mole of calcium and 2x mole of HF exist in the system, x mole of CaF_2 and x mole of H_2 will be decreased as shown in Table 1. Therefore, the molar fraction of each component at equilibrium can be expressed as shown in Table 1. Substituting these values of the molar fractions at equilibrium in Equation 17, the equation becomes the following:

$$\frac{\frac{x}{a}\cdot\left(\frac{2x}{b+x}\right)^2}{\frac{0.1a-x}{a}\cdot\frac{0.01b-x}{b+x}} = \exp\left[-\frac{\Delta G^\circ_{CaF_2} + 2\Delta G^\circ_{HF}}{RT}\right] \quad (18)$$

Knowing the G° and T, x can be solved as a function of a and b. Since the arc atmosphere was assumed to be an ideal gas, the partial pressure of hydrogen is equal to the molar fraction of hydrogen in the arc atmosphere when the total pressure is one. Therefore, substituting x in the following equation, partial pressure of hydrogen can be obtained.

$$P_{H_2} = X_{H_2}\cdot P_T = X_{H_2}\cdot 1 = \frac{0.01b - x}{b + x} \quad (19)$$

Assuming the arc has a cone-shaped geometry, 10 mm in diameter and 10 mm high, and the arc is a closed system, a and b can be estimated as 0.0047 and 1.4×10^{-6}, respectively.

Correlation between Partial Pressure of Hydrogen in the Arc Atmosphere and Dissolved Hydrogen Concentration in Molten Steel

In general, the weld metal diffusible hydrogen content is considered to increase linearly with the square root of the potential pressure of hydrogen in the atmosphere. According to Sievert's law (Refs. 11, 12), the following equation can be written:

$$[H]_{diff} = \alpha\sqrt{P_{H_2}} \quad \text{(Sievert's Law)} \quad (20)$$

where α is the coefficient and a function of temperature. Several researchers have given the value of α. The value given by Christensen (Ref. 11), as indicated in Equations 21 and 22, is the following:

$$[H]_{diff}(ppm) = \alpha_{Christensen}\sqrt{P_{H_2}}(atm) \quad (21)$$

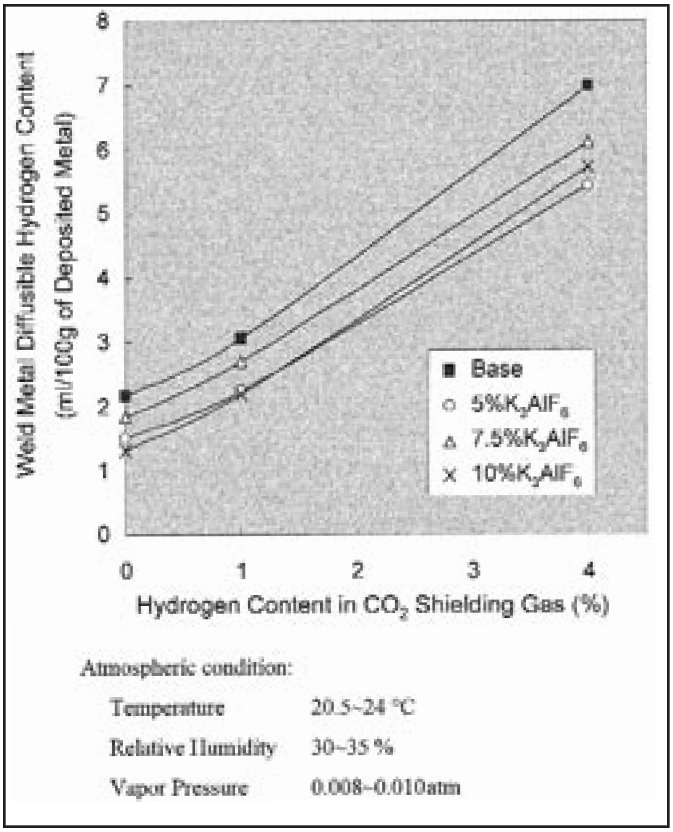

Fig. 4 — Steel weld metal diffusible hydrogen content given by base, 5% K_3AlF_6, 7.5% K_3AlF_6 and 10% K_3AlF_6 wires.

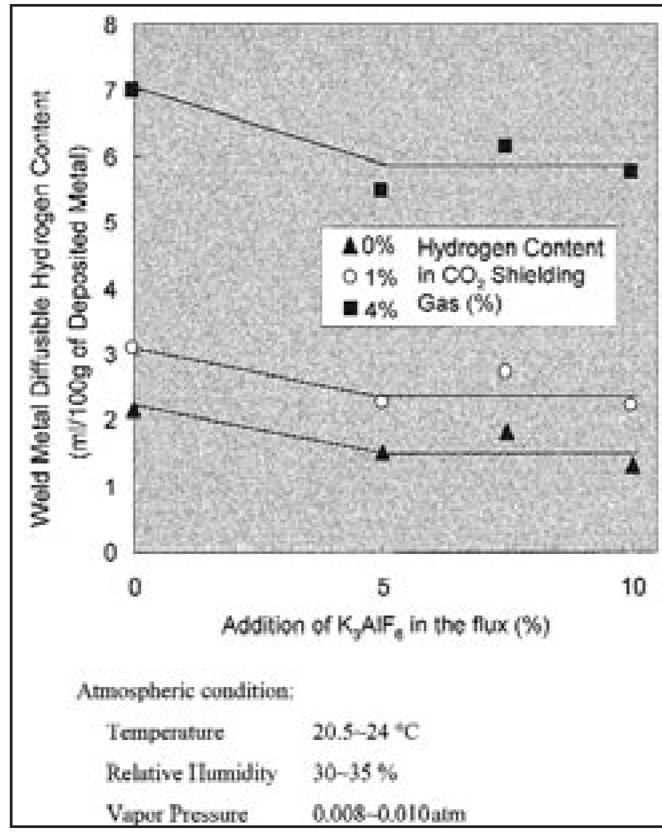

Fig. 5 — Steel weld metal diffusible hydrogen content as a function of the additions of K_3AlF_6 in the fluxes.

$$\log \alpha_{Christensen} = 2.14 - \frac{1550}{T(K)} \quad (22)$$

where T is the temperature of the molten steel. Another was given by Weinstein, *et al.* (Ref. 40), as shown in Equations 23 and 24.

$$[H]_{diff}(ppm) = \alpha_{Weinstein}\sqrt{P_{H_2}}\,(atm) \quad (23)$$

$$\log \alpha_{Weinstein} = 2.41 - \frac{1905}{T(K)} \quad (24)$$

In this work, Weinstein's coefficient was applied to the calculation due to the conservative correlation between diffusible hydrogen and the partial pressure of hydrogen. The final form of diffusible hydrogen, therefore, can be obtained by substituting Equations 23 and 24 to Equation 20.

$$[H]_{diff} = 10^{\left(2.41 - \frac{1905}{T(K)}\right)}\sqrt{\frac{0.01b - x}{b + x}} \quad (25)$$

As can be seen in this equation, the diffusible hydrogen content is a function of T, which is the temperature of the molten steel, and x, which corresponds to the number of moles of HF generated by the reaction at equilibrium. It is obvious an increase in generation of HF will result in lowering the diffusible hydrogen content.

Calculation Process and the Result

The following calculation was developed for the additions of four fluorides, CaF_2, AlF_3, MnF_3 and KF, using the methodology described above. Several additional conditions were also considered for the calculations and are summarized below:

- To fairly examine the effectiveness of fluorides, the atomic fluorine additions to the slag must be adjusted to be constant. Therefore, if the molar fraction of CaF_2 in the slag is 0.1, those of MnF_3 (AlF_3) and KF must be 0.1 x ⅔ and 0.1 x 2, respectively, because the number of fluorine atoms of CaF_2, MnF_3 (AlF_3) and KF in their chemical forms is two, three and one, respectively.
- Taking into consideration the temperature of the weld pool beneath the arc, the reactions are assumed to occur at 2050°C.
- The partial pressure of hydrogen is considered to vary between 0 and 0.04 atmosphere.
- JANAF Thermochemical Table (Ref. 18) and Thermodynamic Properties of Halides (Ref. 19) gave values of standard free energy for the reactions in the calculation.

The calculation results are illustrated in Fig. 1. In this figure, the calculated hydrogen levels for the four fluorides (CaF_2, AlF_3, MnF_3 and KF), and no fluoride additions were plotted as a function of the partial pressure of hydrogen in the arc atmosphere. Here, no fluoride addition indicates the simple correlation of the partial pressure of hydrogen in the arc atmosphere to the diffusible hydrogen content. It is clear the calculated hydrogen levels consistently increased with the partial pressure of hydrogen in the arc atmosphere. All fluorides decreased the hydrogen content when compared with no fluoride addition. A remarkable decrease of the hydrogen level was observed with the addition of CaF_2. Moreover, the addition of AlF_3 demonstrated greater reduction of the hydrogen level when compared with the addition of CaF_2. With the additions of MnF_3 and KF, the respective reductions were incredibly large. However, these values are dependent on the assumptions in the calculations; therefore, they may be different from those observed in practical welding situations.

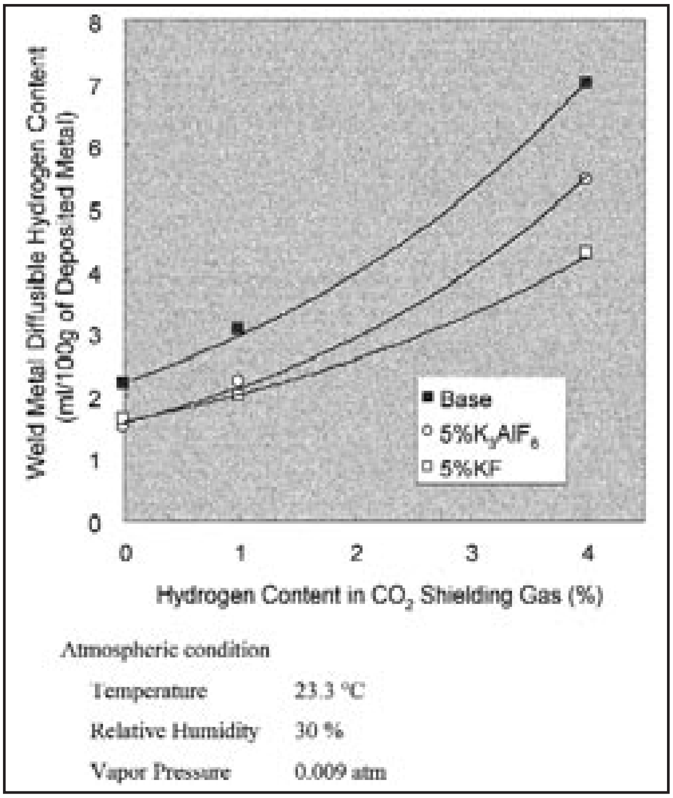

Fig. 6 — Steel weld metal diffusible hydrogen content given by base, 5% K_3AlF_6 and 5% KF wires.

Equilibrium was assumed in the calculation; however, whether the reactions reach equilibrium is questionable because they take place in an extremely rapid manner during welding. Therefore, the kinetics of the reactions that occur between the slag and arc atmosphere must be considered. When the surface area of the slag is larger, the reactions are expected to proceed faster. In the arc, the reaction is considered to take place in two regions: 1) the slag surface covering the molten droplets falling from the electrode to the welding pool, and 2) the slag surface covering the weld pool. Considering the total surface area of the slag, the reaction will occur predominantly in the former region. Once the ions of the fluoride on the surface are depleted because of the reaction, other fluoride ions must be provided to the surface to continue the reaction. The transport of fluoride ions requires diffusion of the species in the slag, which may retard the progress of the reaction. To predict the retardation controlled by the diffusion process, kinetics must be concerned in the calculation. Therefore, the thermodynamic model alone, as introduced in this research, is unable to simulate the precise phenomena that occur in the arc during the welding. Further improvements must be made in the model to quantitatively predict the effectiveness of fluoride additions on reducing the hydrogen level.

In spite of the discussion above, the thermodynamic model was able to predict the relative effectiveness of fluoride additions. For example, according to the calculations, the addition of AlF_3 will decrease the hydrogen level more than that of CaF_2, and the additions of MnF_3 and KF will be more effective than AlF_3. To verify the relative effectiveness of fluoride additions indicated by the calculations, experiments were performed. The results will be shown. In the experiments, the addition of K_3AlF_6 was examined instead of AlF_3 because AlF_3 is considered a hazardous material and difficult to handle. The effectiveness of K_3AlF_6 can be predicted to be somewhere between those indicated by AlF_3 and KF.

Experimental Procedure

Electrode Formulation and Fabrication

Six types of flux cored wires were designed for this research project regarding the additions of different fluorides and their amounts. Their compositions are reported in Table 2. The base electrode formulation was obtained from the fluorspar-lime type basic steel electrodes (E70T-5) reported by Jackson in1973 (Ref. 20). Basic flux composition was selected because it exhibits lower diffusible hydrogen content in the weld metal, compared with acidic- or rutile-based flux. In fact, this flux composition has high CaF_2 content to give high slag basicity, low oxide inclusions and low weld metal diffusible hydrogen. The iron powder content is also high to give better arc stability and high deposition rate. The fluoride (K_3AlF_6, KF and MnF_3) additions were made by substituting a part of CaF_2 in the base formulation without changing the amount of F^- ions in the base formulation. For instance, 5 wt-% of CaF_2 was replaced with 5.5 wt-% of K_3AlF_6 due to the difference of the molecular mass between CaF_2 (78) and K_3AlF_6 (258). To examine the effective amount of fluoride addition, four flux formulations such as base, 5% K_3AlF_6, 7.5% K_3AlF_6 and 10% K_3AlF_6 were designed substituting 0, 5, 7.5 and 10 wt-% of CaF_2 in the base formulation. Zero, 5.5, 8.3 and 11 wt-% of K_3AlF_6 were added respectively. Additionally, to investigate the effectiveness of various fluorides in decreasing weld metal diffusible hydrogen, additions of three different fluorides such as K_3AlF_6, KF and MnF_3 were made by substituting 5 wt-% of CaF_2 with 5.5, 7.4 and 4.8 wt-% of each fluoride, respectively. The weld stability was expected to remain unchanged despite the fluoride additions because the fraction of CaF_2 in these fluxes remained large and the nature of the flux would not be changed. In fact, their explicit deleterious effect was not identified during the experiments.

All the experimental wire electrodes examined in this work were fabricated with the tubular-wire-manufacturing facility at CSM. Figure 2 is a photograph of the tubular-wire-manufacturing facility, which is uniquely designed to produce small batches of wires.

Welding Procedure

The gas metal arc welding (GMAW) procedure was utilized to produce welds with the experimental flux cored wires fabricated at CSM in this research. CO_2 gases including three different levels of hydrogen — 0, 1 and 4% — were used as shielding gas to simulate the atmospheric environments with different hydrogen contents. The welds were performed using a constant voltage power source and direct current electrode positive (reversed polarity) mode. The welding conditions used during all the experiments are shown in Table 3. A heat input equal to 1.4 kJ/mm was maintained in all the experiments.

All the welding experiments were carried out on 12-mm-thick (½-in.) AISI 1010-grade, low-carbon steel plates. This type of steel is recognized as a common structural steel including low carbon content (0.064 wt-%) and low manganese content (0.34 wt-%).

Diffusible Hydrogen Measurement

Diffusible hydrogen content in the weld metal was determined according to AWS A4.3-86, *Standard Methods for Determination of the Diffusible Hydrogen Content of Martensitic, Bainitic, and Ferritic Weld Metal Produced by Arc Welding* (Ref. 22).

Test Assembly and Other Facilities

The test assembly consists of three pieces, the start tab, run-off tab and test piece. The dimensions of the test piece were designed to be 25 x 12 ± 2 mm (1 x ½ in. ± 1/16 in.) and 80 ± 5 mm (3⅛ in. ± ¼ in.), as required by the specification. The dimensions of the start and run-off tabs were designed to be 25 x 12 mm ± 2 mm (1 x ½ ± 1/16 in.) and 40 mm (1 9/16 in.).

All the test assemblies used were degassed for three hours in air at 400°C (750°F) to remove any residual hydrogen in the steel. Subsequently, the assemblies were ground to remove the oxide layer on the surface. Test pieces were then weighed for future use. Just before welding, the assemblies were degreased in acetone.

A test assembly was placed in a copper holding fixture to keep the three pieces in alignment and in intimate contact, and also to extract heat from the assembly. The copper foil seen is used to protect the copper holding fixture from erratic arc strikes.

Test Procedure

A bead-on-plate technique was used to deposit the weld metal on the test assemblies. The arc was initiated on the start tab and continued until reaching in the specified position for the crater on the run-off tab. Within 5 s after extinction of the arc, the test assemblies were removed from the copper fixture and plunged into ice water. The test assemblies were kept in ice water for 30 s while stirring the water. After rinsing with acetone to remove water, the test assemblies were placed into a low-temperature liquid bath of acetone with dry ice or liquid nitrogen.

After the temperature of the low-temperature liquid bath is stabilized, the test assemblies cannot be removed out of the bath for more than 60 s at a time. Therefore, the cleaning of the assemblies was done within 60 s with a sand-blaster to remove any adhered slag and oxide on the test piece. After cleaning, the start and run-off tabs were broken off and the test pieces were placed into the bath.

As recommended by the AWS A4.3-86 specification, the mercury displacement procedure using eudiometer tubes (Fig. 3) was used to measure diffusible hydrogen. As soon as the test pieces were loaded into the eudiometers, they were dipped into a mercury bath and filled with mercury by evacuating from the upper end. The specification (Ref. 22) shows the time from the test piece reaching 0°C to filling the eudiometer with mercury should not exceed 150 s. In case of delay in placing the test pieces in the eudiometers, the results were abandoned.

The mercury baths were placed in a water bath heated at 45°C. At this temperature, it requires 72 h to allow at least 90% of diffusible hydrogen out of the test piece. The amount of diffusible hydrogen collected was measured by reading the scale on the glass tube in the upper part of eudiometer. The measured hydrogen volume should be converted to the value at standard temperature and pressure (0°C [32°F] and 760 mm Hg [14.7 lb/in.^{2}]) by the following equation, as indicated by the specification:

$$VH = \frac{273}{273 + T} * \frac{(P - H) \cdot V}{760} \quad (26)$$

where T is the gas column temperature (°C) at the moment of measurement and can be assumed to be the atmospheric temperature (°C) at the moment of measurement; P is the barometric pressure (mm Hg) at the moment of measurement; V is the measured diffusible hydrogen volume (mL) in the eudiometer; H is the length of the mercury column from the surface of the mercury bath (mm) at the moment of measurement and VH is the volume of hydrogen converted to standard temperature and pressure (mL). In case some liquid was identified above the mercury head in the eudiometer, it was assumed as acetone that remained on the surface of the test piece and the vapor pressure of acetone at the atmospheric temperature at the moment of measurement was subtracted from the barometric pressure (P).

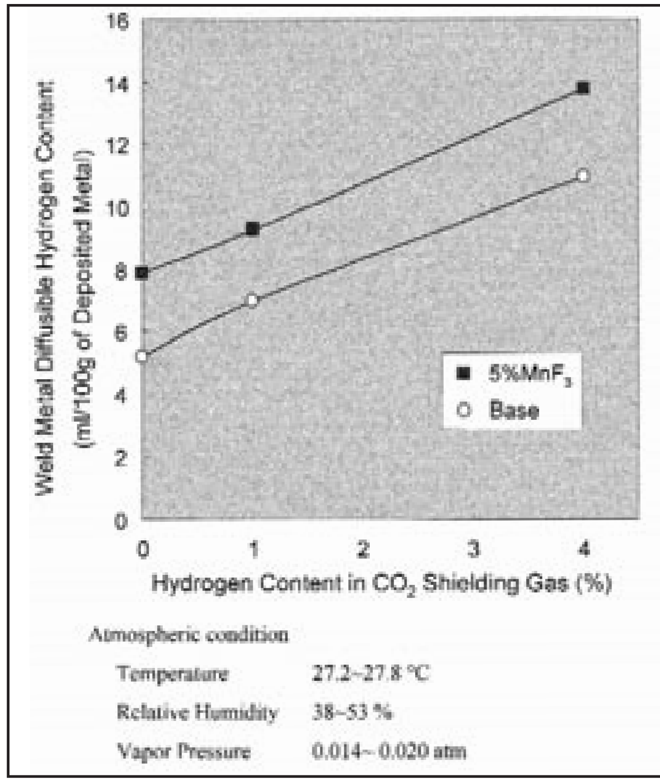

Fig. 7 — Steel weld metal diffusible hydrogen content given by base and 5% MnF_3 wires.

Results and Discussion

Effectiveness of K_3AlF_6 and Influence of the Amount of Its Addition

The thermodynamic calculations previously mentioned have already indicated the effectiveness of the fluorides such as KF and AlF_3. Considering K_3AlF_6 as a mixture of KF and AlF_3, the effectiveness of K_3AlF_6 is expected to be between those of KF and AlF_3, which indicates the effectiveness of K_3AlF_6 would be much greater than CaF_2 but less than KF and MnF_3.

Figure 4 illustrates the experimental results of diffusible hydrogen content in the weld metal deposited with the base wire and the wires with 5% K_3AlF_6, 7.5% K_3AlF_6 and 10% K_3AlF_6 additions. The diffusible hydrogen content increased for all the wires with increasing hydrogen content in the shielding gas. This observation is reasonable because of the increase of partial pressure of hydrogen in the arc atmosphere. Reduction in diffusible hydrogen was observed with each addition of K_3AlF_6. With 5% K_3AlF_6 addition, 30, 27 and 22% of reduction of the diffusible hydrogen were seen at 0, 1 and 4% of hydrogen in the shielding gas, respectively. The reductions were calculated based on the base electrode welds. This observation verified the trend predicted by the thermodynamic calculation, and the addition of K_3AlF_6 is more effective than that of CaF_2 in hydrogen reduction.

Subsequently, the reduction of hydrogen with increasing additions of K_3AlF_6 to the base flux was investigated by measuring the diffusible hydrogen contents of the welds made with the 5% K_3AlF_6,

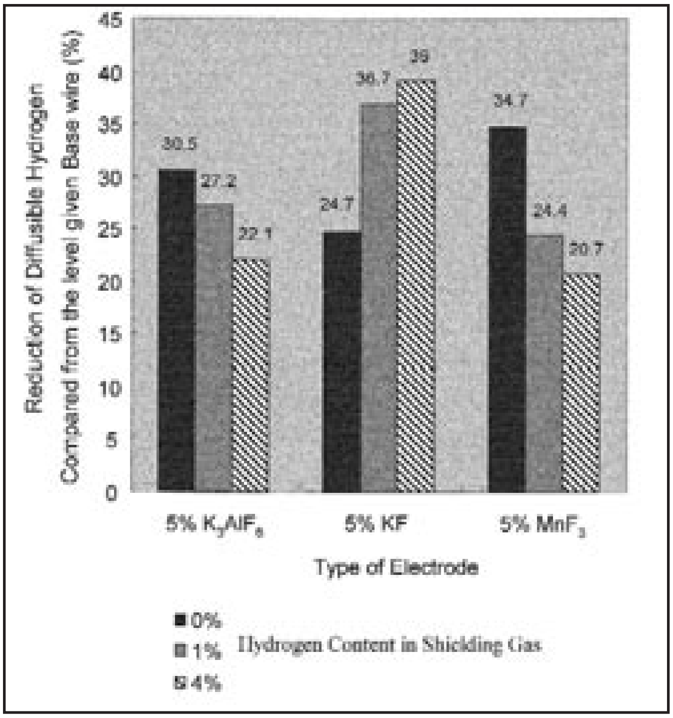

Fig. 8 — Reduction of diffusible hydrogen from the levels given by base electrode established with 5% K_3AlF_6, 5% KF and 5% MnF_3 wires.

7.5% K_3AlF_6 and 10% K_3AlF_6 wires. If the amount of K_3AlF_6 in the flux is increased, the diffusible hydrogen content is expected to decrease. However, further reduction of the diffusible hydrogen was not observed simply with increasing the addition of K_3AlF_6 beyond 5%. The diffusible hydrogen contents measured in welds prepared with 7.5% addition were between those given by the base wire and the 5% K_3AlF_6 wire at any hydrogen addition in the shielding gas. Also, the hydrogen content measured in welds prepared with 10% addition of K_3AlF_6 is as low as that with 5% addition at each hydrogen content in the shielding gas. Moreover, this observation indicates the reduction of the diffusible hydrogen by the addition of an effective fluoride such as K_3AlF_6 probably reached a plateau when the addition exceeded an optimal amount, which was determined to be 5% in this research. Figure 5 illustrates the same experimental results as those in Fig. 4 plotted as a function of the fluoride addition. The three curves show hydrogen additions in the shielding gas resulted in increased weld metal diffusible hydrogen content. The drop of the diffusible hydrogen is clearly observed from 0 to 5% of the fluoride addition and no further reduction resulted from additions of more than 5%.

According to the series of the diffusible hydrogen measurements with the K_3AlF_6 wires, the optimum addition of the effective fluoride was determined to be 5% in the flux so that it was applied to the addition of other fluorides such as KF and MnF_3.

Effectiveness of KF

According to the thermodynamic calculations demonstrated earlier, the addition of KF is predicted to be more effective than the addition of K_3AlF_6. As seen in Fig. 1, the addition of KF exhibits the greatest reduction of hydrogen so that the hydrogen level is very close to zero at even 0.04 atmosphere of partial pressure of hydrogen, which is high compared to normal welding atmospheres.

The diffusible hydrogen experiments were conducted with 5% KF addition wire to verify the effectiveness of KF as predicted by the calculation. The results are illustrated in Fig. 6. At 0% hydrogen in the shielding gas, the diffusible hydrogen content in the weld metal deposited with the 5% KF addition wire is as low as in the weld metal deposited with the 5% K_3AlF_6 addition wire. However, with a higher hydrogen content in the shielding gas, the weld metal diffusible hydrogen levels of 5% KF addition wire tend to be lower than those of base and 5% K_3AlF_6 addition wires. Compared with the 5% K_3AlF_6 addition wire, the reductions of the diffusible hydrogen with the 5% KF addition wire were 13.1 and 21.8% at 1 and 4% of hydrogen in the shielding gas, respectively. Consequently, it can be concluded the addition of KF can further reduce diffusible hydrogen. This fact matches the result of the thermodynamic calculation.

Effectiveness of MnF_3

The thermodynamic calculation demonstrated earlier also indicated the effectiveness of MnF_3. As seen in Fig. 1, the reduction of the hydrogen shown by the addition of MnF_3 is close to that shown by the addition of KF.

The results of the diffusible hydrogen measurements with 5% MnF_3 addition wire were illustrated in Fig. 7. The hydrogen levels shown in this figure are much higher than those shown in the previous figures because the temperature and relative humidity at the time when these diffusible hydrogen measurements were performed (27.5°C, 38–53% RH) were higher than those when the other measurements were conducted (23.3°C, 30% RH). Since the partial pressure of hydrogen becomes higher when both temperature and humidity increase, the diffusible hydrogen level will be higher in an environment with higher temperature and humidity. This fact makes it impossible to simply compare the values of the diffusible hydrogen levels conducted under different environmental conditions. Therefore, the effectiveness of the addition of MnF_3 needed to be evaluated by calculating the reductions of the diffusible hydrogen levels for the experimental wires containing K_3AlF_6, KF and MnF_3 with respect to those of the base electrode. The reductions were also normalized according to the following equation:

$$\frac{[H]_D(\text{base}) - [H]_D(\text{experimental})}{[H]_D(\text{base})} \times 100 = \text{reduction}(\%) \tag{27}$$

where $[H]_D$(base) is the weld metal diffusible hydrogen level of the base wire and $[H]_D$(experimental) is that of the other experimental wires containing K_3AlF_6, KF and MnF_3. Figure 8 illustrates the reduction given by the three fluoride-added electrodes with 5% K_3AlF_6, 5% KF and 5% MnF_3, respectively. On average, the addition of KF shows the largest reductions of 24.7, 36.7 and 39.0% at 0, 1 and 4% of hydrogen content in shielding gas, respectively. The reductions given by the addition of MnF_3 are 34.7, 24.4 and 20.7% at 0, 1 and 4% of hydrogen content in shielding gas, respectively. These reductions are approximately as large as those given by the addition of K_3AlF_6, whose reductions are 30.5, 27.2 and 22.1% at 0, 1 and 4% of hydrogen content in shielding gas, respectively. Consequently, it is obvious the addition of MnF_3 is as effective as or more effective than K_3AlF_6 in decreasing the diffusible hydrogen.

The thermodynamic calculation has indicated the effectiveness of the additions of KF and MnF_3 would be much greater than that of K_3AlF_6. Moreover, KF would be slightly more effective than MnF_3 according to the calculations. Therefore, the reduction of the hydrogen should be greater with KF, MnF_3 and K_3AlF_6, in that order. The experimental results followed this trend. Although the predicted hydrogen levels for these three fluorides did not exactly match the diffusible hydrogen levels observed in the experimental results, it is still meaningful to be able to predict the relative effectiveness of fluorides in reducing the hydrogen level.

In addition, it can be seen the trend of the diffusible hydrogen reduction as a function of hydrogen content in the shielding gas is different for the different fluorides, as shown in Fig. 8. For K_3AlF_6 and MnF_3 additions, the diffusible hydrogen reduction decreased as the hydrogen content in the shielding gas increased. On the other hand, KF addition showed greater reduction of the diffusible hydrogen with increasing hydrogen content in the shielding gas. This trend cannot be explained at this point; however, it may indicate the KF addition is more effective in reducing the diffusible hydrogen when the partial pressure of hydrogen is large in the arc atmosphere.

Conclusions

The major achievements of this investigation can be summarized in the following conclusions:

- The effectiveness of K_3AlF_6, KF and MnF_3 in lowering hydrogen in steel weld metal is shown by preliminary thermodynamic calculation and experimentation.
- A 5% addition of K_3AlF_6 was more effective than a 10% addition in controlling weld metal diffusible hydrogen content.
- Additions of K_3AlF_6, KF and MnF_3 at 5% resulted in 22 to 30%, 35 to 40% and 21 to 35% of diffusible hydrogen reductions, respectively.
- KF addition was more effective in reducing the diffusible hydrogen when the partial pressure of hydrogen is larger in the arc atmosphere, while K_3AlF_6 and MnF_3 additions showed smaller reduction of diffusible hydrogen at higher hydrogen content in the shielding gas; however, the mechanism was not clarified.

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