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Effects of Fluoride in the Flux on Hydrogen Content in Weld Metal and Operating Behavior in FCAW-S

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Abstract

Various fluorides, CaF_2, K_2SiF_6, NaF, and LiF were added to self-shielded flux cored arc welding wires and their effects on the diffusible hydrogen content in the weld metal and the operating behavior were compared. Because of their easier vaporization and active reactions with hydrogen in the arc, K_2SiF_6, NaF, and LiF were more effective than CaF_2 in reducing hydrogen content in weld metals. Even if slag basicity was varied from 1.92 to 2.53 depending on the fluoride added, no clear relationship was observed between the slag basicity and the hydrogen content, implying that a small variation of slag basicity has little influence on the hydrogen content in FCAW-S, which generates a large amount of gas during welding. The wires with K_2SiF_6, NaF, and LiF gave a more aggressive and violent arc, and resulted in a larger amount of spattering, especially large size spatters, than the wire with CaF_2. It is believed that excessive volumes of vaporized gas in the wires with K_2SiF_6, NaF, and LiF hinder droplet detachment and lead to droplet of larger sizes. Moreover, the wires with K_2SiF_6, NaF, and LiF produced somewhat rough and irregular surfaces, having a slightly inconsistent bead height and width, resulting in restricted current and voltage ranges within which they can operate satisfactorily.

Key Words : FCAW-S, Hydrogen, Fluoride, Arc stability

1. Introduction

Because of the easy access to the root region with a narrow gap, the self-shielded flux cored arc welding[1] (FCAW-S) process is often used in root welding. However, as stresses are concentrated at the root region, the possibility of the occurrence of hydrogen cracking should be considered when the process is used in root welding. To prevent hydrogen cracking, diffusible hydrogen content in the weld metal should be minimized[2]. Fluorides such as calcium fluoride (CaF_2) have been used as one of the main flux ingredients in FCAW-S wires to minimize the contamination of molten metal by air and hydrogen. It has been reported[3,4] that the fluorine produced by the dissociation of the fluoride added reduces the hydrogen partial pressure in the air and reacts with the hydrogen to form hydrogen fluoride (HF), which is insoluble in the molten metal. Several research works have been carried out to find more effective fluorides in various welding processes. Matsushita and Liu[5] demonstrated that the replacement of CaF_2 with KF, MnF_3, and K_3AlF_6 in flux cored arc welding (FCAW) wires resulted in less diffusible hydrogen content in weld metals. Similar observations have also been reported in shielded metal arc welding (SMAW). Du Plessis *et al*[6] reported that a 20% substitution of CaF_2 with NaF in the electrode resulted in approximately a 25% decrease in hydrogen. It has also been reported[7-9] that the slag basicity, which is dependent on the flux formulation, influences the diffusible hydrogen content in the weld metal. Tsuboi and Terashima[7,8] examined the hydrogen content in weld metals in submerged arc welding (SAW) by altering the slag basicity, and observed that the hydrogen content decreased with an increase of slag basicity. Bang *et al.*[9] reported a similar effect of slag basicity on the hydrogen content in FCAW.

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In addition to the effect on the hydrogen content, flux ingredients, especially fluorides, also influence the operating behavior in welding processes. It is known[10] that the addition of fluorides in SMAW electrodes results in a harsh arc and a more convex bead shape, and produces higher levels of spatter. Compared to the works on the effect of fluorides on the hydrogen content, research on the effect on the operating behavior, especially in FCAW-S, have seldom been performed. In this work, various fluorides, CaF_2, K_2SiF_6, NaF, and LiF were added to FCAW-S wires and their effects both on the hydrogen content in the weld metal and on the operating behavior were compared.

2. Experiments

Four experimental FCAW-S wires (1.6 mm in diameter), equivalent to AWS E81T1-K2, with different alkaline or alkaline earth fluorides, CaF_2, K_2SiF_6, NaF, and LiF, were fabricated, utilizing raw materials typically used in the commercial production of FCAW-S wires. The amount of each fluoride added to the flux was 10 wt. %. Except for the fluorides, the amounts of all other flux ingredients, such as calcite ($CaCO_3$), dolomite ($CaCO_3 \cdot MgCO_3$), lithium silicate ($Li_2O \cdot SiO_2$), and iron powder were the same in all wires.

The diffusible hydrogen content in the weld metals was determined according to AWS A4.3-86[11]. The test specimens were assembled in a copper welding fixture and welded. The welding parameters were maintained at 220A-23V-18cm/min. After measuring the amount of weld metal hydrogen, the values were corrected for the standard temperature, atmospheric pressure, and humidity conditions. The values were reported in terms of 100g deposited metals.

The effects of the fluorides on the arc stability and spatter generation were also investigated. Three bead-on-plate welds of 300 mm in length each were prepared using the same welding parameters in a copper chamber and the spatters generated during welding were collected and weighed after separating them from the slag particles magnetically. The spattering ratio, which is the ratio between the weight of the spatters and the weight of the deposited metal, was used as an indication of the arc stability. Spatters collected were also classified to determine size distribution. During welding, the arc voltage and current signals were also monitored using a high-speed data acquisition system with a 5 kHz data sampling frequency. The standard deviations of the arc voltage were calculated and used as an indication of the arc stability. After welding, the welds were sectioned in the transverse direction to the welding and the profiles of the weld beads were observed.

3. Results and Discussion

Table 1 shows the result of the determination of diffusible hydrogen content in the weld metals. The diffusible hydrogen content of weld metal A, which was produced from the wire with CaF_2, was 14 mL/100 g. Weld metals B, C, and D that were produced from the wires with K_2SiF_6, NaF, and LiF showed diffusible hydrogen contents of 9.68, 8.9, and 9.39 mL/100 g, respectively. This indicates that K_2SiF_6, NaF, and LiF are more effective in reducing diffusible hydrogen content than CaF_2 in FCAW-S. As explained in the introduction, it has been reported that K_2SiF_6 and NaF are more effective in reducing hydrogen content than CaF_2 in FCAW[5] and SMAW[6]. In addition to the two fluorides, LiF was shown to be more effective than CaF_2 in this experiment.

In the previous work[5], it was claimed that the reason for the reduced hydrogen content by K_2SiF_6 and NaF in the weld metals was their easier vaporization and active reactions with hydrogen in the arc. Thermodynamic analysis was conducted to confirm that LiF has the same characteristics as those of K_2SiF_6 and NaF. The equilibrium constant of the vaporization reaction of LiF was calculated and compared with that of CaF_2. Fig. 1 shows the result of this comparison. The result for NaF is also included in the figure for comparison. The Fig. 1 shows that the equilibrium constant of the vaporization

Table 1 Diffusible hydrogen contents in weld metals

Weld metal	Diffusible hydrogen content(mL/100g)				
A	14.21	13.28	14.52	14	(14)*
B	9.56	9.92	9.47	9.75	(9.68)
C	9.78	8.28	8.64	8.89	(8.9)
D	9.67	9.56	9.18	9.16	(9.39)

*average value in parenthesis

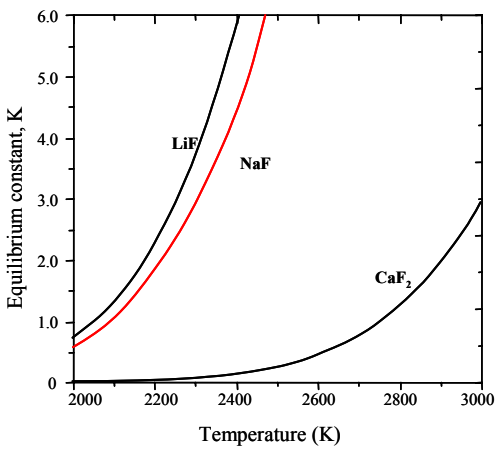

Fig. 1 Equilibrium constants of vaporization reactions of fluorides

reaction of LiF is much higher than that of CaF_2, indicating that LiF is vaporized more easily to form gaseous LiF than CaF_2. After vaporization, the gaseous LiF tends to react with hydrogen to form HF. The equilibrium constant of the reaction between gaseous LiF and hydrogen to form HF was also calculated. As hydrogen presents as a diatomic or monatomic form in the arc, depending on the arc temperature, the following two reactions should be considered.

$$2LiF\ (g) + H_2\ (g) = 2HF\ (g) + 2Li\ (g) \quad (1)$$

$$K = \frac{a^2_{HF(g)} \cdot a^2_{Li(g)}}{a^2_{LiF(g)} \cdot a_{H_2(g)}}$$

$$LiF\ (g) + H\ (g) = HF\ (g) + Li\ (g) \quad (2)$$

$$K = \frac{a_{HF(g)} \cdot a_{Li(g)}}{a_{LiF(g)} \cdot a_{H(g)}}$$

Fig. 2 shows the results of these reactions. Irrespective of the hydrogen form, the values for the reactions between gaseous LiF and hydrogen are greater than those for the reactions between gaseous CaF_2 and hydrogen. The above results indicate that, in addition to NaF and K_2SiF_6, LiF is also more effective than CaF_2 in FCAW-S because of its easier vaporization and active reaction with the hydrogen to form in the to form HF in the arc.

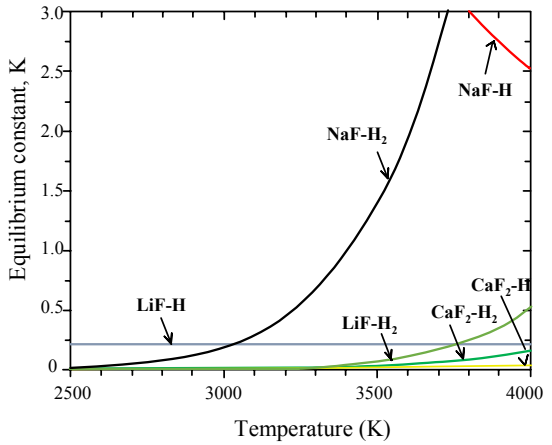

Fig. 2 Equilibrium constants of reactions between gaseous fluorides and hydrogen to form HF

As fluorides also act as slag formers, in addition to the effects on vaporization and reaction with the hydrogen, the effects of fluoride on slag basicity should also be considered. It is known that hydrogen content in molten metal is strongly dependent on the water vapor solubility, *i.e.* the hydroxyl capacity, in the slag. According to Ban-ya *et al.*[12], when basic slag is formed, the hydroxyl capacity in the slag tends to increase, resulting in reduced hydrogen content in the molten metal. To investigate the effect of slag basicity on the hydrogen content in the weld metal in this experiment, the chemical composition of the slag in each weld metal was determined and the basicity was calculated using the equation proposed by Tuliani *et al.*[13]. Table 2 shows the chemical compositions and basicities of slags in all weld metals. All weld metals have basic slags with basicity ranging from 1.92 to 2.53. Fig. 3 shows the relationship between the slag basicity and hydrogen content in the weld metal. Hydrogen content varied little or even increased with an increase of basicity. This indicates that, even if different slag basicities are produced in this experiment, hydrogen content in the weld metals is not influenced by the slag basicity. Because external shielding gas is not used in FCAW-S, a large amount of gas generation ingredients such as calcium carbonate is added in the FCAW-S wire, producing a large amount of gas. Under this circumstance, it is be-

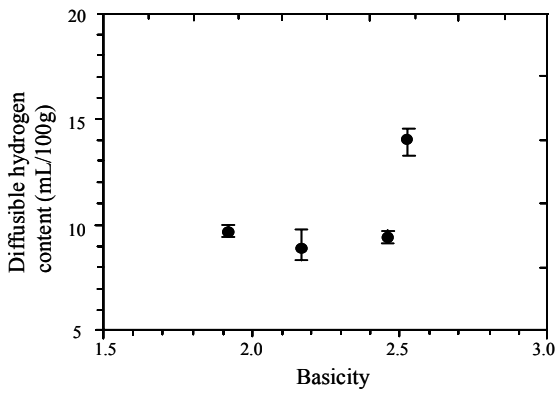

Fig. 3 Relationship between slag basicity and diffusible hydrogen content in weld metal

Table 2 Chemical compositions of slags (wt. %)

Weld metal	CaF_2	CaO	Na_2O	MgO	Al_2O_3	SiO_2	K_2O	TiO_2	MnO	FeO	ZrO_2	BaO	Li_2O	Basicity*
A	8.00	16.21	0.32	24.41	40.76	0.86	0.05	0.95	0.37	4.81	1.95	0.17	5.64	2.53
B	5.08	7.00	0.15	26.15	42.40	2.50	0.43	1.59	0.59	11.26	1.96	0.05	4.24	1.92
C	7.30	3.60	3.09	26.95	42.16	1.20	0.05	1.32	0.84	9.21	1.69	0.06	5.58	2.17
D	9.12	4.07	0.31	25.85	40.81	0.86	0.05	1.03	0.57	8.35	1.82	0.08	11.95	2.46

*Basicity = {CaO + MgO + CaF_2 + Na_2O + K_2O + (MnO + FeO) + BaO + Li_2O + SrO}/{SiO_2 + (Al_2O_3 +TiO_2 + ZrO_2}

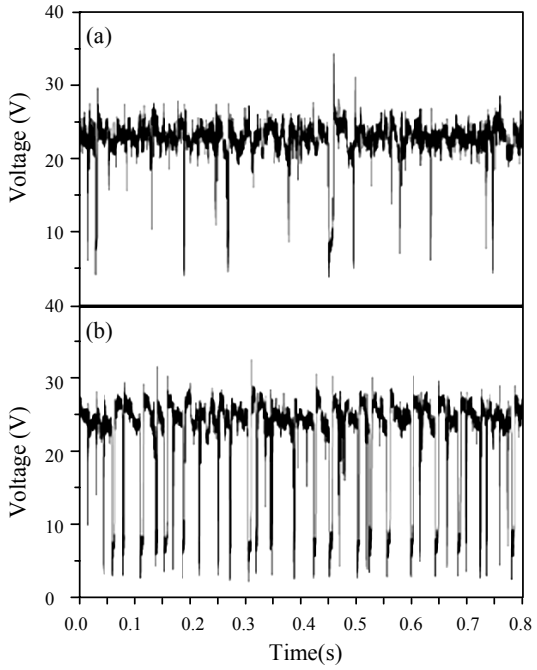

Fig. 4 Typical arc voltage signals from the wires (a) with CaF_2 and (b) with LiF

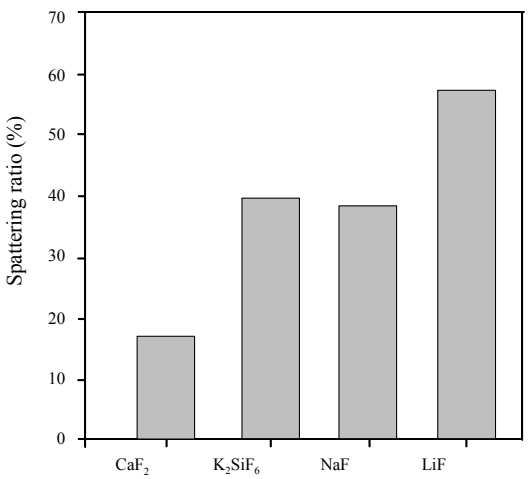

Fig. 5 Comparison of spattering ratio between wires with different fluorides

lieved that the small variation of slag basicity, 1.92-2.53, observed in this experiment has little influence on the hydrogen content in the weld metals.

Arc stability was examined by observing the change in arc voltage and by measuring the amount of spattering. In general, an unstable arc leads to a larger amount of spattering. As explained in the experimental procedures, the electrical arc signals were monitored using a high-speed data acquisition system and the amount and size distribution of spatters collected were determined. It showed that, compared to the arc voltage trace from the wire with CaF_2, traces from the other wires are quite

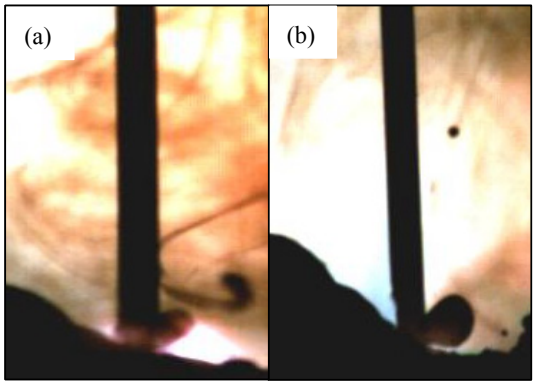

Fig. 6 Comparison of droplet formations between (a) the wires with (a) CaF_2 and (b) the wire with LiF

erratic. Fig. 4 shows typical arc voltage traces from the wires with CaF_2 and LiF as examples. The standard deviation of arc voltage in all wires was determined. While the standard deviation of arc voltage was 2.74 V for the wire with CaF_2, it was 5.86, 6.45, and 6.33 V for the wires with K_2SiF_6, NaF, and LiF, respectively. Fig. 5 compares the spattering ratios among wires. In comparison to 16.97 % for the wire with CaF_2, it was 39.58, 38.24, and 57.28 % for the wires with K_2SiF_6, NaF, and LiF, respectively. These results indicate that wires with K_2SiF_6, NaF, and LiF give a more aggressive and violent arc, and thus result in a larger amount of the spattering than the wire with CaF_2.

A high-speed camera was operated to observe the droplet formation during welding. It showed that droplets in all wires are suspended outside the axis of the wire. However, the droplets in the wires with K_2SiF_6, NaF, and LiF were larger than the droplet in the wire with CaF_2. Fig. 6 compares the droplets in the wires with CaF_2 and LiF as examples. According to Killing[14], this type of droplet formation in FCAW-S may result from gas formation from the wire. He explained that if vigorous gas formation is produced from the wire, a gas cushion is formed below the droplet which supports the droplet and prevents its detachment. In this circumstance, the droplet increases in size and turns around the wire probably due to the turbulence of the gas generated. This concurs with the above thermodynamic analysis, in which K_2SiF_6, NaF, and LiF are shown to be vaporized more easily than CaF_2. It is believed that excessive volumes of vaporized gas in the wires with K_2SiF_6, NaF, and LiF hinder droplet detachment and lead to droplets of larger size. This argument can be supported by the measurements of the size distribution of the spatters. Fig. 7 compares the size distribution of spatters between the wire with CaF_2 and the wire with LiF. While the proportion of spatters that are larger than 1.0 mm was about 90 % in the wire with LiF, it was

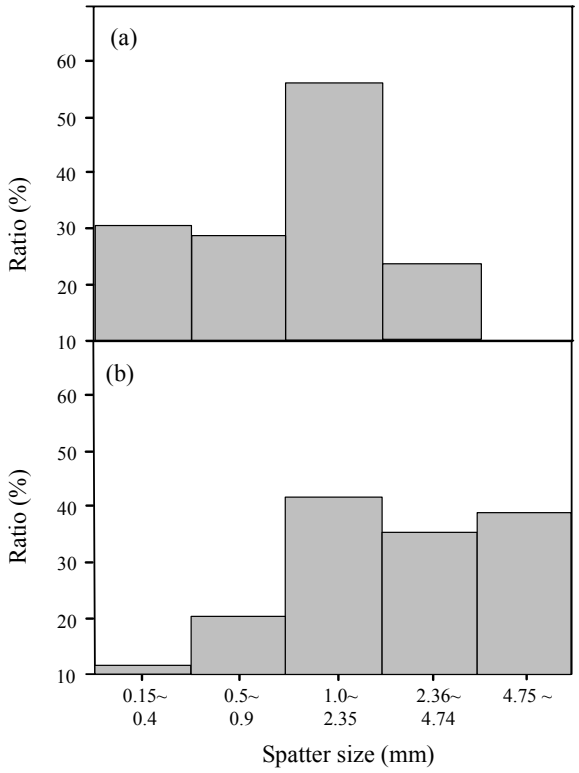

Fig. 7 Comparison of size distribution of spatters between (a) the wire with CaF_2 and (b) the wire with LiF

about 60 % in the wire with CaF_2.

The surface finish and profile of the weld beads were also observed. The wire with CaF_2 produced beads that were smooth in appearance with a uniform bead width and height. However, other wires produced beads with somewhat rough and irregular surfaces having a slightly inconsistent bead height and width. Moreover, some instances showed poorly crowned beads and undercutting, indicating a lack of fluidity. Fig. 8 compares the cross sections of beads from the wires with CaF_2 and LiF. The edges of the beads produced by the wire with CaF_2 flowed smoothly into the base plate at a low angle of contact. However, the bead produced by the wire with LiF shows a crowned bead because of low fluidity. By varying the arc voltage and current, the operating window for each wire was established and compared. The window was bound by conditions which produce poor weld quality, viz lack of penetration, excessive bead width, excessive bead height, and undercutting. It showed that wires with K_2SiF_6, NaF, and LiF have a smaller window than the wire with CaF_2. The wire with NaF has the smallest window. Fig. 9 compares the windows between the wire with CaF_2 and the wire with NaF. It indicates that the wire with NaF has restricted current and voltage ranges within which they can operate satisfactorily.

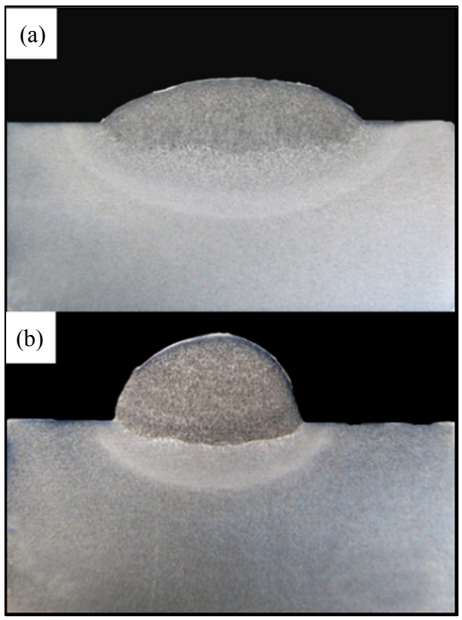

Fig. 8 Comparison of cross section of beads between (a) the wire with CaF_2 and (b) the wire with LiF

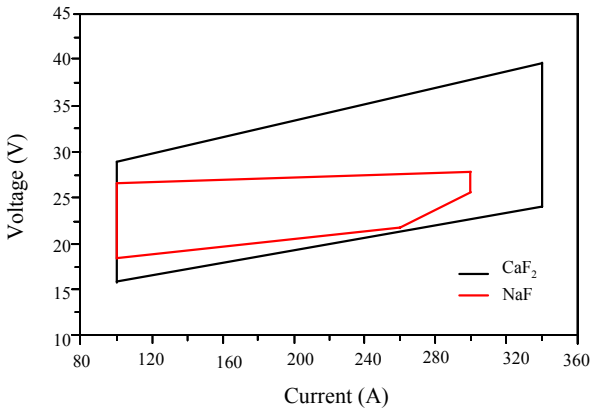

Fig. 9 Comparison of operating windows between the wire with CaF_2 and the wire with NaF

4. Conclusion

Various fluorides, CaF_2, K_2SiF_6, NaF, and LiF were added to FCAW-S wires and their effects both on the diffusible hydrogen content in the weld metal and on the operating behavior were compared. The important results obtained are as follows:

1) Because of easier vaporization and active reactions with hydrogen in the arc, K_2SiF_6, NaF, and LiF were more effective than CaF_2 in reducing hydrogen content.

2) Even if slag basicity was varied from 1.92 to 2.53 depending on the fluoride added, no relationship was observed between the slag basicity and the hydrogen content in the weld metals, suggesting that a small variation of slag basicity has little influence on the hydro-

gen content in FCAW-S, which generates a large amount of gas.

3) Wires with K_2SiF_6, NaF, and LiF gave a more aggressive and violent arc, and resulted in a larger amount of spattering, especially large size spatters, than the wire with CaF_2. It is believed that excessive volumes of vaporized gas in the wires with K_2SiF_6, NaF, and LiF hinder droplet detachment and lead to droplets of larger size.

4) The wires with K_2SiF_6, NaF, and LiF produced somewhat rough and irregular surfaces, having a slightly inconsistent bead height and width, resulting in restricted current and voltage ranges within which they can operate satisfactorily.

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