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Some Considerations on State of Flourine Ion in Flux †

Nobuya IWAMOTO*, Yukio MAKINO** and Norimasa UMESAKI***

Abstract

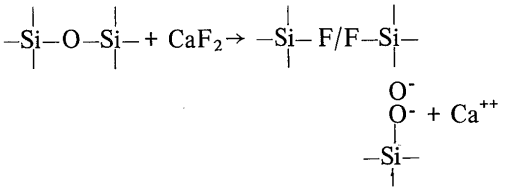
State of flourine ion in silicate melt was investigated by several spectroscopic methods. Infrared absorption study could not make clear on the state of flourine ion, but it was determined that the intensity of absorption near 780cm^{-1} increased with increasing CaF_2 content in the system $xCaF_2 \cdot (1-x)CaO \cdot SiO_2$. In the chemical shift study using ESCA, fairly clear results were obtained in this system. These results seem to reject the formation of Si–F bond that has been predicted in previous studies. Likewise, emission X-ray peak shift was found in the system CaF_2–CaO–SiO_2. Further investigation are desired because detailed discussion was impossible on account of insufficient data at present.

1. Introduction

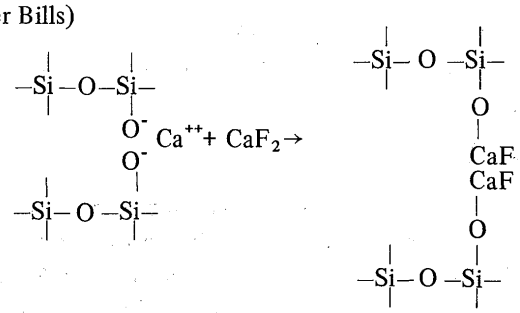
Flouride in flux, for examle CaF_2 or KF, is generally used to improve weldability. Although prevention of water vapour dissolution in slag or improvement of arc stability has been achieved from the addition of CaF_2 or KF in flux, roles of flouride added, especially, behaviours of flourine ion in slag have been not clarified in welding process. In general, it is thought that in flourosilicate SiF_4 or HF gas is produced from the reaction between slag components or between slag and water vapour in atomosphere. Therefore, further investigation for utilities of flouride is aquired from environmental standpoint.

In previous works as to formation of flourosilicate, the formation of Si–F bond has been discussed with infrared absorption measurement and with changes of various physical properties by flouride addition. It was first report that Kozakevitch discussed the formation of CaF_2–Al_2O_3–SiO_2 from viscosity measurement.[1] Bills also measured viscosity about the system CaO–Al_2O_3–SiO_2 containing CaF_2.[2] They suggested following structural changes respectively.

(after Kozakevitch)



(after Bills)



Kumar, Ward and Williams presented that absorption at 855 cm^{-1} is attributed to the formation of Si–F bond with infrared absorption studies.[3),4)] However, Mitchell gave the interpretation that new absorption band did not appear even if $(Si_3O_9F)^{-7}$ ion was formed with flouride addition.[5)]

Up to the present time, state of flourine ion in flourosilicate melt has been mostly studied with physical properties measurements and infrared absorption method. In this paper, state of flourine ion in some silicate slags has been studied with several spectroscopic means.

2. Experimental procedures

Sample slags were prepared from reagent grade SiO_2, alkaline-earth carbonate and flouride by mixing them in a mortar and porcelain pestle. After all specimens were melted at the temperature of 100°C higher than those melting points and kept for 0.5 hr or 1hr in platinum crucible in resister-type furnace, they were taken out into air and cooled.

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Infrared absorption spectra were measured in the range from 450 cm^{-1} to 4000 cm^{-1} with KBr dilution method. The apparatus used was a spectrometer of 225 type (Hitachi Co., Ltd.).

The experimental conditions for X-ray emission study were as follows:

Target : Rh K_α, Voltage and Current : 50kV x 60mA

Crystel : TAP, Path : Vaccum, P.H.

CaF_2 was used to establish the standard angular position of the flourine Kα radiation. The angular shift, $\Delta^\circ(2\theta)$, of the flourine Kα peak for specimens was determined from the equation

$\Delta^\circ(2\theta) = {}^\circ(2\theta)\,(CaF_2) - {}^\circ(2\theta)(\text{specimen})$

ESCA spectra were measured on the following conditions:

Target : Al K_α Voltage : 9kV,

Scanning rate : 0.05v/sec, Sensitivity : 100cps or 200cps

3. Infrared absorption

Although it is anticipated that flourides would take similar behaviours to alkali or alkaline-earth metal oxides in silicate melt[6], its behaviour remains unclear. State of flourine ion in silicate melt has been often discussed in previous works and the formation of Si–F bond or solvating effect of flouride[7] is a subject of discussion.

The shift of absorption near 1000 cm^{-1} was attributed to the formation of unbridged oxygen by addition of alkali or alkaline-earth metal oxide.[8] If flouride behaves as modifier perfectly, the role of one molecule of flouride corresponds to that of two molecules of oxide modifier for the formation of unbridged oxygen. Therefore, the shift of absorption near 1000 cm^{-1} increases with increasing flouride content when modifier oxide is exchanged with corresponding flouride. The shift was slight in $xCaF_2\cdot(1\text{-}x)CaO\cdot SiO_2$ slags as shown in Fig. 1. However, it is the noticeable result that the absorption near 780 cm^{-1} appears with increasing flouride content. Kumar et al. observed an absorption at 855 cm^{-1} in the system CaF_2–CaO–SiO_2.[9] They considered that the absorption was attributed to Si–F bond. However, Mitchell indicated the fact that the absorption at 855 cm^{-1} was attributed to crystalline rankinite($3CaO\cdot 2SiO_2$)[10] The origin of the absorption observed in this study seems different from that of the absorption at 855 cm^{-1} because samples used in this study were identified as amorphous state with X-ray diffraction method.

Absorption spectra containing various flouride are shown in Fig. 2. It will be seen that the stronger the

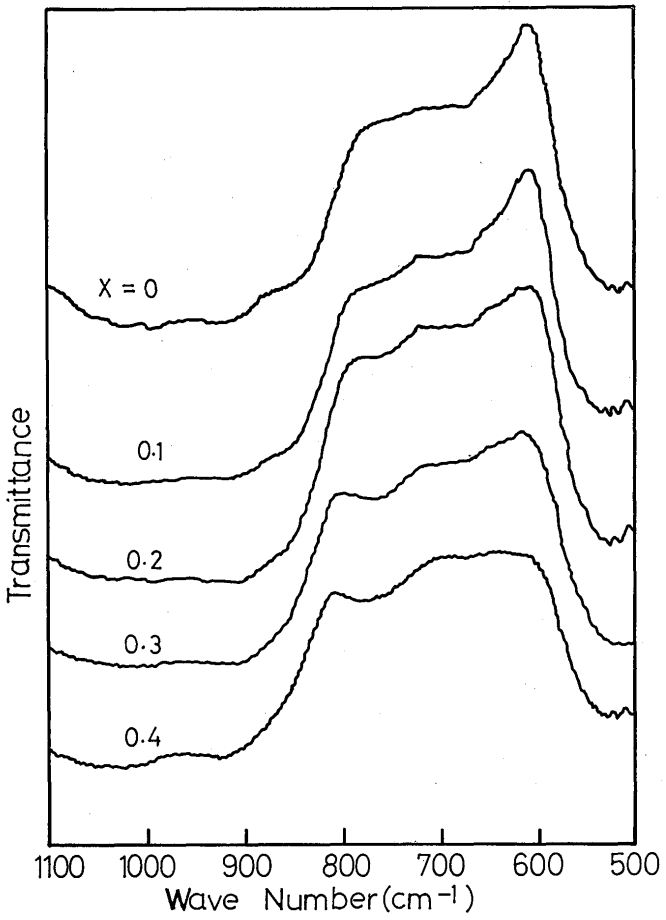

Fig. 1 Absorption spectra of slags in the system $xCaF_2\cdot(1-x)CaO\cdot SiO_2$

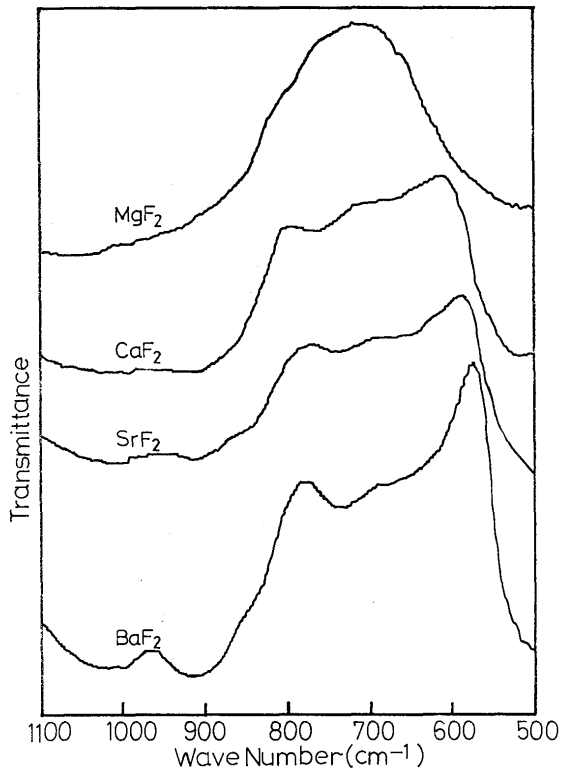

Fig. 2 Absorption spectra of $0.3MF_2\cdot 0.7MO\cdot SiO_2$ slags (M ; Mg, Ca, Sr, Ba)

polarizing power of divalent cation in slag is, higher wave number absorption appears.

The absorption near 800 cm^{-1} can be observed as very weak in vetreous silica and strong in quartz and other crystalline silicate. The absorption has often been interpreted with occurrence of ring ions, for example, $(Si_3O_7)^{2-}$.[11),12)] In silica glass it is also considered that the absorption is attributed to asymmetry of SiO_4 group.[13)] Infrared absorption results gave unclear conclusion as to the formation of Si–F bond or solvating effect of flouride in silicate slag. The absorption near 780 cm^{-1} would not be related to the formation of Si–F bond but to the increase of degree of asymmetry in SiO_4 groups due to flouride addition.

4. Chemical shifts in ESCA and emission X-ray spectroscopy

As is generally known, energy state of electron sensitively changes corresponding to change in the crystal field. In ESCA, binding electron is released by X-ray radiation and the binding energy of released electron is obtained with measurement of its kinetic energy. On the other hand, characteristic X-ray of atoms composed of compound is measured in emission X-ray spectroscopy. Change in the crystal field gives a shift of energy level of electron and reflects as chemical shift in ESCA as well as emission X-ray spectroscopy.

(i) Chemical shift in ESCA[14),15)]

Generally, electronegativity of surrounding atoms is believed as the most effective factor to chemical shift. The larger electronegativity of surrounding atoms becomes, the more electrons of noticed atom are attracted to neighbouring atoms and the larger effective charge arround its nucleus becomes. Thus it will be interpreted that chemical shift in ESCA depends on the difference of effective charge arround the nucleus.

When noticed atom is cation, the larger electronegativity of neighbouring anions becomes, the more effective charge of nucleus of cation increases. Thus, potential field of cation nucleus becomes stronger because average electron density of cation decreases and energy spectrum of electron released from cation shifts in higher energy. On the contrary, the larger electronegativity of neighbouring cations becomes in the case of anion, the more effective charge of anion nucleus decreases. Thus, potential field of anion nucleus becomes weaker and energy spectrum of electron released from anion shifts in lower energy.

ESCA spectra of F_{1s} and Si_{2p} in the system $xCaF_2 \cdot (1\text{-}x)CaO \cdot SiO_2$ and their peak positions are shown in Figs. 3, 4 and 5, respectively. Their peak positions were measured at half value width. Although the slight

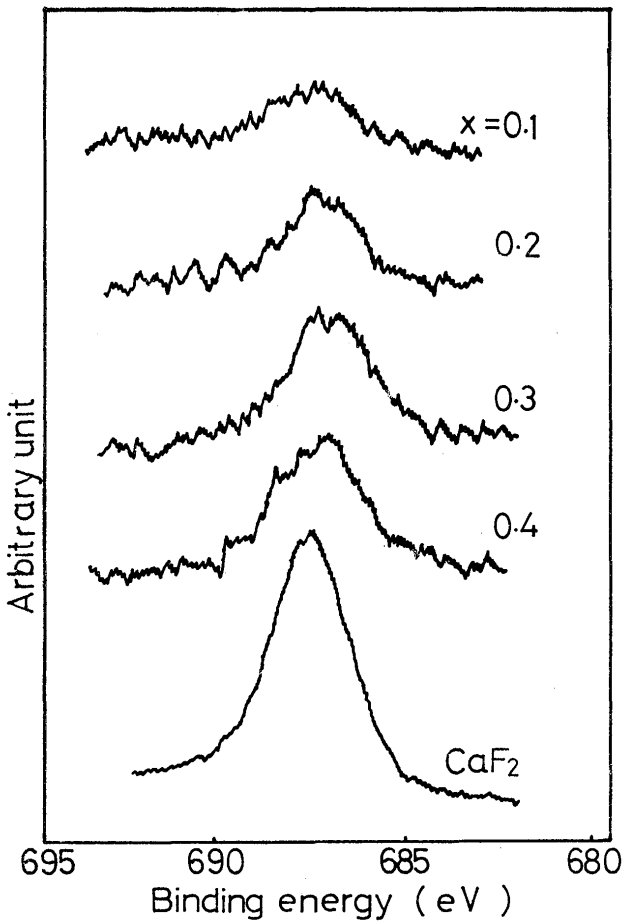

Fig. 3 F_{1s} ESCA spectra of slags in the system $xCaF_2 \cdot (1-x)CaO \cdot SiO_2$

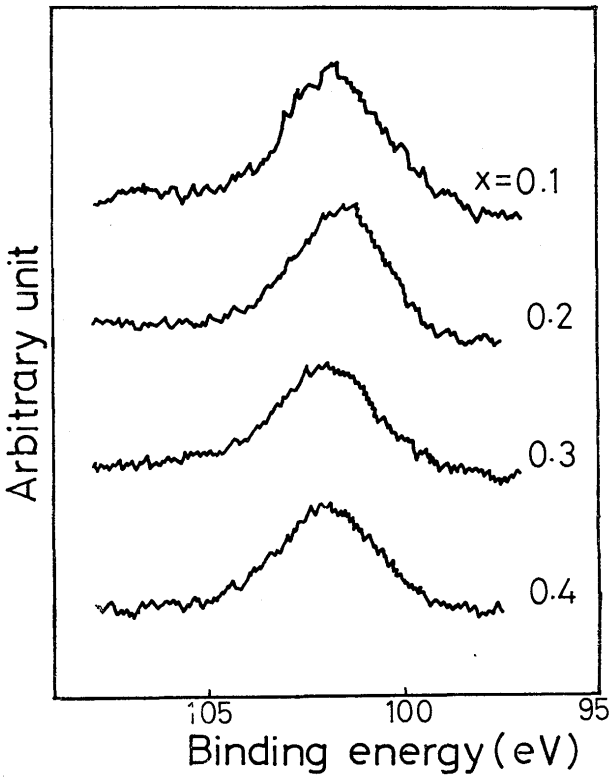

Fig. 4 Si_{2p} ESCA spectra of slags in the system $xCaF_2 \cdot (1-x)CaO \cdot SiO_2$

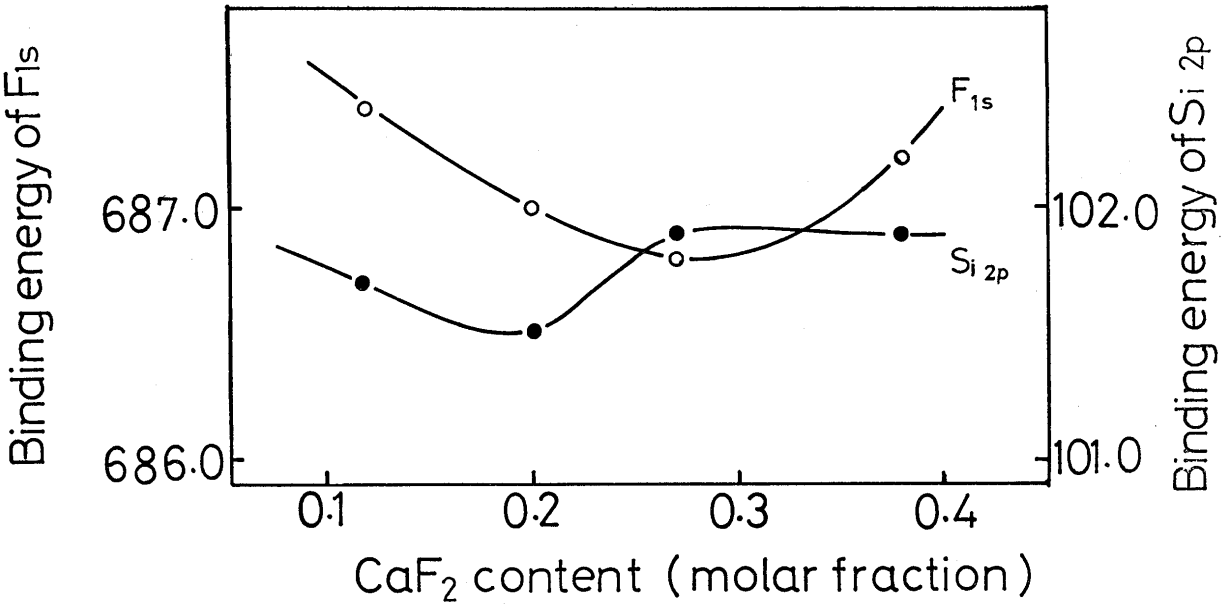

Fig. 5 Dependence of F_{1s} and Si_{2p} binding energy on CaF_2 content

shift was obtained in Si_{2p} spectra, the shift of F_{1s} spectra was fairly remarkable.

If Si–F bond is formed in slag, the effective charge of Si nucleus becomes larger than that in Si–O bond because χ_F is larger than χ_O (χ_F and χ_O are electronegativities of flourine oxygen ion, respectively). Therefore, ESCA spectrum of Si_{2p} is believed to shift in higher energy. On the other hand, spectrum of F_{1s} is also believed to shift in higher energy becuase χ_{si} is larger than χ_{ca} and effective charge of flourine nucleus in Si–F bond is larger than that in Ca–F bond. According to the result, it must be considered that Si–F bond is not formed in the system. Formation of O–Ca–F bond rather than that of Si–F bond must be anticipated from the shifting behaviour of F_{1s} spectrum because effective charge of flourine nuclues in O–Ca–F bond is smaller than that in F–Ca–F bond.

(ii) Chemical Shift in emission X-ray spectroscopy[16), 17)]

Chemical shift in slags of the system CaF_2–CaO–SiO_2 was measured with changing CaO/SiO_2 ratio under constant 10 wt% CaF_2. In Table 1, it was showed that chemical shift decreased with decreasing

Table 1 Chemical shift of X-ray emission spectra

Sample composition		$\Delta^\circ 2\theta$
CaO/SiO_2=40/60	CaF_2=1owt%	0.021
45/55	10	0.034
50/60	10	0.037
55/45	10	0.037

CaO/SiO_2 ratio. Although clear explanation was impossible at present on account of insufficient data, it is supposed that state of flourine ion depends on basicity of slag.

5. Vaporization of flourine and change of refractive index

Flourine ion in flourosilicate is believed to evaporate in the form of HF or SiF_4. The result of chemical analysis of flourine and silicon in slag is shown in Table 2. Silicon loss was under 4 mole% as shown in Table 2. Therefore, it can be thought that in the system $xCaF_2 \cdot (1\text{-}x)CaO \cdot SiO_2$ evaporation of flourine occurs in the form of HF.

Table 2 The result of checmial analysis of slags in $xCaF_2 \cdot (1-x)CaO \cdot SiO_2$

CaF_2 mole fraction	heating time (min)	Si loss in slag (%)	F loss in slag (%)
X=0.1	30	0	0
0.2	30	1.6	0.2
0.3	10	1.6	0.2
	20	1.6	2.5
	30	0.4	3.0
	40	1.1	9.2
0.4	30	4.2	2.1

Refractive index of specimen well reflects the change of flourine content as shown in Fig. 6. Although vaporization loss of flourine sensitively corresponds to the treating temperature and the holding time, this result suggests that the difference of these experimental conditions gives effect on the refractive index of specimen. It seems appropriate that the refractive index

can be used as a measure of flouride content in slag.

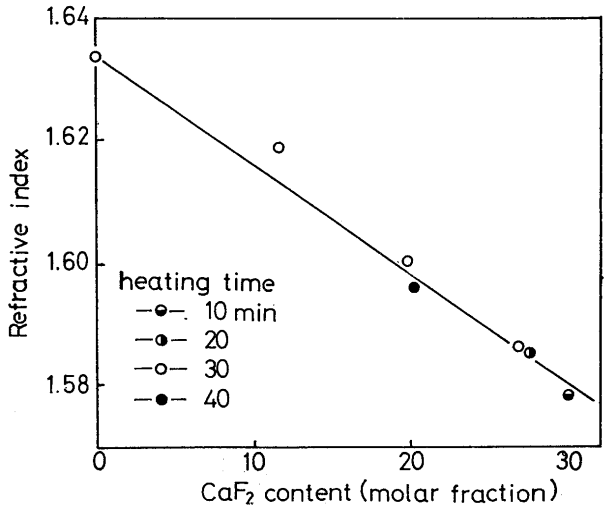

Fig. 6 Dependence of refractive index on CaF_2 content

Summary

State of flourine ion in flourosilicate was investigated with infrared absorption, ESCA and emission X-ray spectroscopy. Infrared absorption study could not make clear on the state of flourine ion in slags of the system $xCaF_2 \cdot (1\text{-}x)CaO \cdot SiO_2$, but it was determined that the absorption near 780 cm^{-1} appeared with increasing CaF_2 content. The results of chemical shift in ESCA could be qualitatively interpreted with the difference of electronegativities of nearest neighboring atoms. According to this interpretation, it seems to reject the formation of Si–F bond in slags of the system $xCaF_2 \cdot (1\text{-}x)CaO \cdot SiO_2$. Chemical shift in emission X-ray study was also observed in slags of the system CaF_2—CaO–SiO_2. From this result, it is supposed that state of flourine depends on basicity of slag. However, clear explanation was impossible at present on account of insufficient data.

Acknowledgement

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