Infrared Emission Spectra of Molten Slags

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ABSTRACT

Infrared emission spectra of molten $CaO-CaF_2-SiO_2$ was directly measured. by combining hot thermocouple technique and FTIR. Emission for those related to Si-O bond observed in this *in situ* observation. Si-F emission could not be found in the present condition.

1. INTRODUCTION

The vibrational spectra of molten slag, glass and salt is one part of structural information. However, to observe molten state of substances, high temperature experiment is necessary. Therefore, for experimental simplicity works been reported were for the "quenched (rapidly solidified)" slags, glasses and salts. Very few have been reported on the direct measurement of molten slags but Kusabiraki et al[1)]for sodium silicate.

Techniques of infrared spectra measurement have been used in earlier studies would be summarized as: absorption, reflection, attenuated total reflectance spectroscopy(ATR) and emission spectroscopy. Details review may be found elsewhere[2)].

Emission spectroscopy was chosen in the present investigation because direct signal from molten sample could be obtained. Use of this technique has been reported by Kozloeski[3)], Bates and Boyd[4)], and, Kusabiraki and Shiraishi[5,6,7,)]. Kozloeski[3)] obtained the emission spectra of molten alkali metal nitrates. But the spectrum obtained were rather unclear. The emission spectra of molten alkali metal nitrates reported by Bates and Boyd[4)] were clear and good in quality, however, it is difficult application for high temperature measurements.

Kusabiraki and Shiraishi obtained the transmission spectra of alkali metal carbonates[5)] and alkali metal silicates[1,6,7)] by combining two spectra emitted by thin and thick layer of specimen. This technique, however, would require a relatively large hot chamber and complex optical systems. Since this type of measurement is very difficult, it may conceive error doing the analysis of data.

Thus, each of these methods suffers respectively inherent disadvantage. Therefore, simple and easy technique for measuring spectrum is very much needed. In the author's report, a new technique which is the combination of infrared emission spectroscopy and hot-thermocouple technique, was proposed. The new technique was then applied to the measurement of the spectrum of molten alkali-metal nitrates[2)]. Spectra obtained for various nitrates were the sharpest of the kinds and agreed with those measured by the conventional complicated techniques[8)].

In this report, results of infrared spectroscopy of molten nitrates are summarized to verify the technique and the tests for the molten $CaO-CaF_2-SiO_2$ system are presented.

2. THEORETICAL ASPECT

The theoretical consideration of emission of the light could be found in the refrence2). Here a brief explanation is made. An emission of light from a plane at distance x parallel to the substrate toward outside is schematically shown by arrow A in Figure 1, where d is thickness of the sample, R is reflectivity at the interface between the sample and environment, R_2 is reflectivity at the interface between sample and substrate (platinum in the present study), k is absorption coefficient of the materials. The absorption of the sample (t) for thickness d will be exp(-kd).

$$t = \exp(-kd) \quad \cdots\cdots\cdots\cdots\cdots\cdots(1)$$

In this analysis, the effect of temperature and wave length on the emission and reflection were omitted for simplicity.

The radiation from the layer at x repeats reflection and reabsorption between sample surface and substrate interface. The radiation from the layer at x decay by exp(-kx), and reaches at sample surface. At sample surface, a part of radiation is returned inside by reflection and the residue goes out of the surface. Such reflection and reabsorption are repeated.

The radiation emitted from the layer at X toward the sample-substrate interface is also presented as B in Figure 1. Same treatment could be done for this side. Consequently, the total emission leaving the surface is given by a sum of integrated between limits of 0 and d. Therefore;

$$\begin{aligned} J &= j\cdot(1-R)\cdot(1+R\cdot R_2 t^2 + R^2\cdot R_2^2\cdot t^4 \\ &\qquad + \cdots)\cdot\int_0^d \exp(-kx)dx \\ &\quad + j\cdot(1-R)\cdot(R_2\cdot t + R\cdot R_2^2\cdot t^3 + R^2 R_2^3\cdot t^5 \\ &\qquad + \cdot\cdot)\cdot\int_0^d \exp[-k(d-x)]dx \\ &= \frac{j}{k}\cdot\frac{(1-R)\cdot(1-t)\cdot(1+R_2)}{(1-R\cdot R_2\cdot t^2)} \quad \cdots\cdots\cdots\cdots\cdots\cdots(2) \end{aligned}$$

Since relative emissivity ε_s is defined as

$$\varepsilon_S = \frac{J}{J_B} = \frac{J}{\left(\frac{j}{k}\right)} \quad \text{.................(3)}$$

Substitution of equation (3) into (2) yields

$$\varepsilon_S = \frac{(1-R)\cdot(1-t)\cdot(1+R_2\cdot t)}{(1-R\cdot R_2\cdot t^2)} \quad \text{.............(4)}$$

Since substarate is mirror polished platinum, R_2 may be set to unity. Hence,

$$\varepsilon_s = \frac{(1-R)\cdot(1-t^2)}{(1-R\cdot t^2)} \quad \text{.................(5)}$$

If absorption coefficient and sample thickness is small enough kd could be considered to be far smaller than unity. Substituting t=1-kd and letting Rt^2 to R and k^2d^2 to 0 yields

$$\varepsilon_s \cong 2kd \quad \text{................(6)}$$

Thus, for a transparent and thin sample, we can obtain absorption like emission spectra.

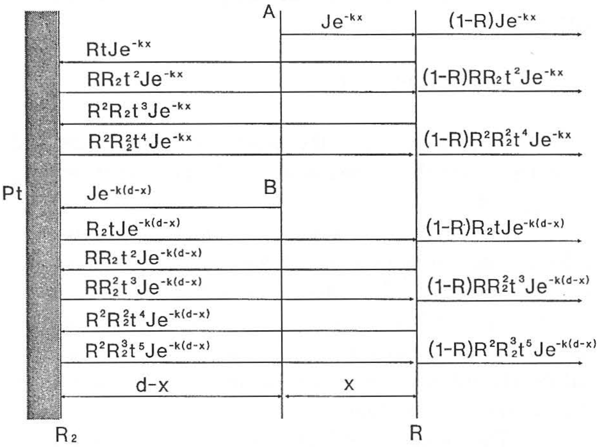

Figure 1 Schematic of light emitted in the molten slag at position x. Light A is emitted toward surface and B to the substrate.

3. EXPERIMENTAL APPARATUS

3.1 Hot-thermocouple technique

In hot-thermocouple technique, the thermocouple itself also serves as a heating element, support for the sample, and measuring temperature. This technique is therefore suitable for determining melting characteristics of various materials[9,10,11)]. There are three methods for hot-thermocouple technique[12,13,14)]. In this study, a technique reported by Yanagase et.al[14)] was used.

3.2 Cell for Measurement

The hot-thermocouple cell was so designed that a measurement could be done in the spectrometer. A schematic diagram of the hot-thermocouple cell is shown in Figure 2. Cell is made of brass and the outer diameter is 80mm. The window is of KBr poly-crystal of 35mm diameter. Gas inlet and outlet were mounted to introduce various gas in the cell for controlling atmosphere.

The thermocouple used for the heating filament is Pt-6%Rh/Pt-30%Rh thermocouple. This filament of the thermocouple can measure up to 1650°C. The junction of the filament was made flat and mirror polished prior to the experiment. Samples was the plane on that the flat junction.

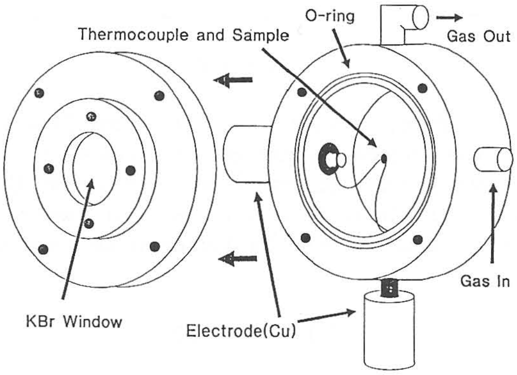

Figure 2 Cell design for emission measurement

3.3 FT-IR

The Fourier Transform Infrared Spectrometer model JIR-100(JEOL) was used in this study. The cell was placed in front sample room. The radiation from a sample directly enters in the interferometer without specially designed optical system. A MCT type detector was used for the measurements and the spectral region is between 600 cm^{-1} and 4000 cm^{-1} with the resolution of up to 0.0625 cm^{-1}.

3.4 Experimental Procedure

The sequence of experiment was (1)heating the filament above the melting point of sample and emission measured, then (2) heating the filament with a sample and measure the sample emission under an exactly same condition for the background.

The resolution used for most measurements was 4 cm^{-1} and scan was made for 500 times. The ratio of the sample emission spectrum to the background emission spectrum was then computed, and the result was plotted as the relative emissivity of the sample.

Reagent grade chemicals were used for the whole experiment.

4. RESULT OF PRELIMINARY MEASUREMENT (NITRATE EMISSION[2])

A emission spectrum of the filament without sample including background was used as a reference and a emission spectrum with molten $LiNO_3$ was compared with the reference. Obtained relative emissivity of $LiNO_3$ from the ratio of these two spectra is shown in Figure 3.

The frequencies and assignment of the bands in this study and those obtained by other technique are presented in Table. Present results were in good agreement with the results with other technique. Therefore, this technique is a reasonable tool for measuring emission spectrum of molten salt, slag and glass.

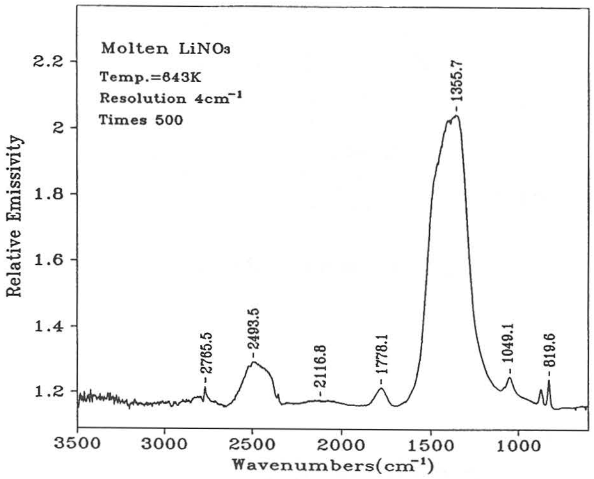

Figure 3 Measured relative emissivity of $LiNO_3$ at 643K

5. RESULTS FOR CAO-CAF$_2$-SIO$_2$ MOLTEN SLAGS.

Slag composition studied are shown in Figure 4 in ternary phase diagram. Premelted slag was prepared prior to the experiment and composition was chemically analyzed. Argon atmosphere was employed for all measurement.

5.1 Resolution and emission spectrum

Effect of resolution was examined prior to the experiment. Emission spectra at various resolutions of spectrometer(from 0.25 to 4 cm^{-1}) were examined for molten slags of CaO-CaF_2-SiO_2 at 1723K. Resolution of the spectrometer did not affect the shape, structure and the position of the absorption. Resolution of 4 cm^{-1} is sufficient for the high temperature measurement.

5.2 Time dependent of emission spectrum

Since this system contained CaF_2, evaporation of specimen may affect the spectrum because of the so small amount of sample on the filament. Spectrum for the slag of $XCaO/XCaF_2=0.14$, $SiO_2=8.1$ mass% was continuously measured from 10 to 320 seconds at 1732K. Relative emissivity at 870 cm^{-1} was plotted in Figure 5. There was no change in the absorption nor the position of the peak. One measurement of 500 times accumulation takes 50 second, therefore, composition change of specimen during measurement is negligible under present experimental condition.

5.3Emission spectrum and temperature

Same slag was tested for the effect of temperature for the spectrum (Figure 6). According to the phase diagram reported, melting point of the slag is estimated to 1632K. Liquid slag was quenched on the copper plate and used as a starting materials. Spectrum for the quenched sample was also shown for the reference.

In the spectrum for quenched sample at room temperature by KBr pellet technique, there exist absorption at 950 and 870 cm^{-1}. At 1273K emission at 870 remained but that of 950 disappeared. At 1473K, spectrum is broader but 950 appeared again while 870 still remains. At both temperature slag is solid and the spectrum gradually loses its two clear peaks. At 1723K, slag is molten, the spectrum has no more two peaks but one broader band at 900 cm^{-1}.

Initial slag was prepared at 1723K and then quenched. The melting point of the slag of this

Table Wave-number (cm^{-1}) in the literature and those of observed

$LiNO_3$		$NaNO_3$		KNO_3		$RbNO_3$		$CsNO_3$		Assignment
Ref.	Obs.	Ref.	Obs.	Ref.	Obs.	Ref.	Obs.	Ref.	Obs.	
2820	2766	2770	2766	2750	2766	2745	2766	2720	2766	$2\nu_3$
2440	2439	2415	2424	2400	2393	2390	2395	2380	2372	$\nu_1+\nu_3$
2160	2117	2070	2059	2070	2054	2060	2044	2050	2038	$2\nu_1$
1770	1778	1765	1765	1755	1755	1750	1753	1745	1741	$\nu_1+\nu_4$
1328	1356	1330	1342	1325	1338	1320	1330	1318	1323	$\nu_3(E')$
1050	1049	1048	1049	1045	1045	1041	1043	1039	1038	$\nu_1(A'_1)$
820	819	826	825	830	829	830	829	830	829	$\nu_2(A''_2)$
735	730	730	719	720	713	710	692	710	707	$\nu_4(E')$

composition was estimated about 1632K. With the characteristics in emission spectra, the quenched specimen shows similar spectra with that of at 1423K. Structure at about the temperature may reserved in the quenched specimen. At 1273K the structure frozen in the specimen relaxed and stabilized showing a shifted spectrum to that of quenched.

5.4 Effect of silica content on the spectrum

Silica content was varied from 0.2 to 8.1 mass% at the ratio $XCaO/XCaF_2=0.14$ (Figure 7). In all composition studied, there was a similar peak at 900 cm^{-1}. The height of the peak increases with increasing the silica content. At higher silica content emission at 1030 cm^{-1} is fairly observed. Emission at 870 cm^{-1} could also be seen.

For the slag composition at the ratio $XCaO/XCaF_2=0.68$, spectra were obtained as in Figure 8. Emission was observed around 870 cm^{-1}. Increasing in silica content decreases height of shoulder at about 950 cm^{-1} and the spectra become more clear. According to similarity of spectrum with those of the ratio $XCaO/XCaF_2=0.14$, structure of silicate anion in these composition seems similar.

Slag of the ratio $XCaO/XCaF_2=1.56$ also showed a similar but slightly different spectrum (Figure 9). Silica content was varied from 8 to 40 mass%. Up to 25 mass% silica, the broad emission at 870 cm^{-1} was observed. Increasing silica to 40 mass% emission at higher wave number increased. At 830 cm^{-1} there exists an emission and increased with increasing silica content. Emission at 950 was also found and at the highest silica composition emission at 1030 cm^{-1} was observed

For reference pure fused silica was tested by same technique (Figure 10). Emission at 1030 cm^{-1} is attributable to the vibration of Si-O-Si in complete SiO_4 tetrahedron and 783 cm^{-1} is that for symmetric stretching.

Characteristic emission in the slag studied were found to be 830, 870, 950 and 1030 cm^{-1}. In the compositional triangle the symbolic expression for these emissions are plotted in Figure 11. The line for the CaO/SiO_2 ratio is drawn to the end of stable silicates, namely C_3S, C_2S, C_3S_2 and CS.

Emission at 1030 cm^{-1} was observe for the slag containing more silica than the line to CS. And less slica composition than the line to C_2S, emission at 950 cm^{-1} observed. The 870 and 830 cm^{-1} emission was observed for all composition studied.

According to Kusabiraki's report[1] 950 cm^{-1} is assigned to Si-O-Si (bridged) and 860 cm^{-1} is that of Si-O-(non-bridged) in alkali silicate. If their assignment is valid for the present condition, bridged silicon-oxygen bond may exist for solid state, however, in the liquid slag of same composition it may not exist or at least the population of this type of bond decreased. Instead, Si-O-non bridged bond is still observed and population seems about same.

Raman spectroscopy was applied to molten alkali silicate[16]. The absorption observed was at 1100, 970, 920 and 870 cm^{-1}. Comparison with that of crystal, they assigned those to one to four non-bridging oxygen respectively in silicate tetrahedron. Although infrared emission and Raman spectroscopy obeyed different selection rule, similar explanation may be applied and present results agreed qualitatively.

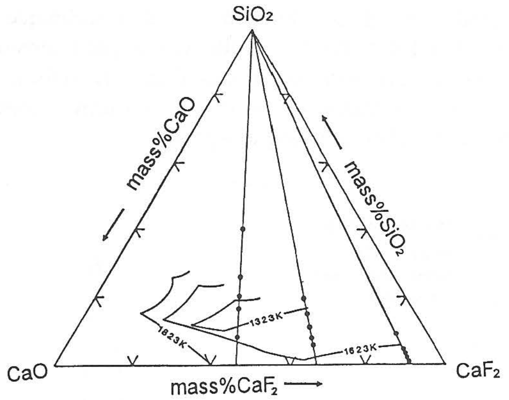

Figure 4 Slag composition studied

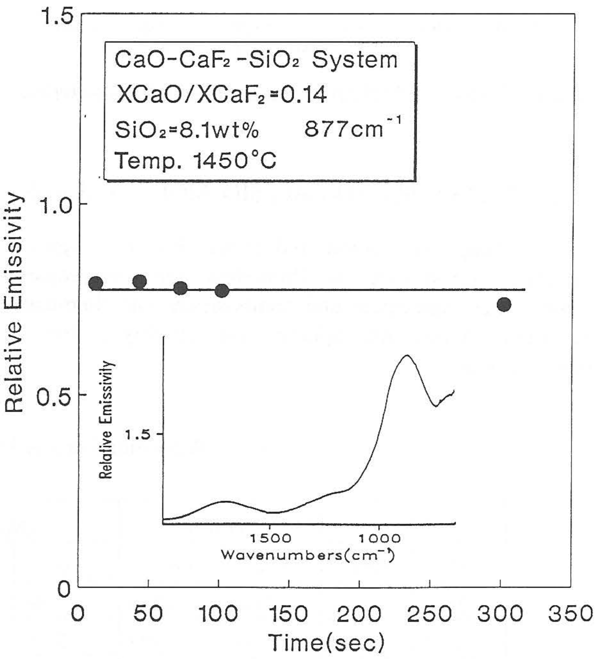

Figure 5 Intensity of emission at 877 cm^{-1} as a function of time.

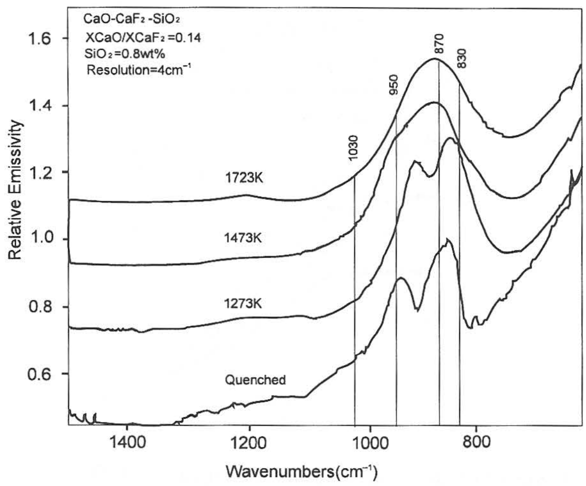

Figure 6 Effect of temperature on the spectrum

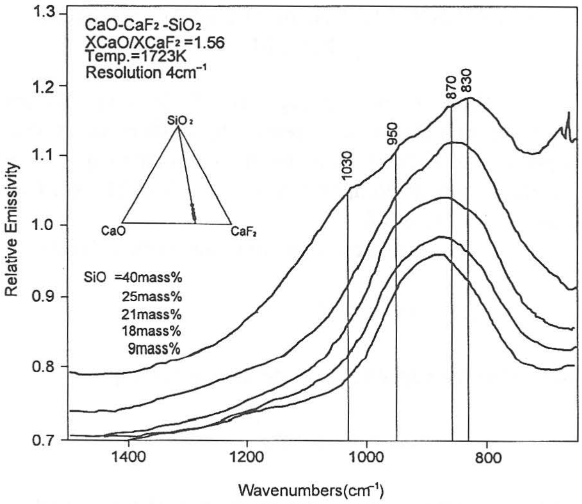

Figure 9 Emission spectra of molten slags with various silica content from 9 to 40 mass% at the ratio XCaO/XCaF$_2$=1.56

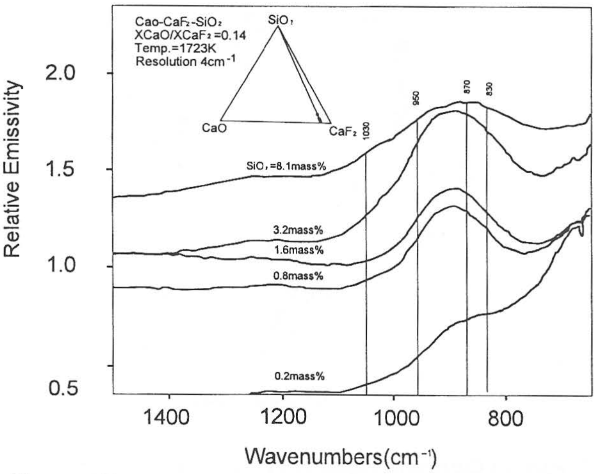

Figure 7 Emission spectra of molten slags with various silica content from 0.2 to 8.1 mass% at the ratio XCaO/XCaF$_2$=0.14

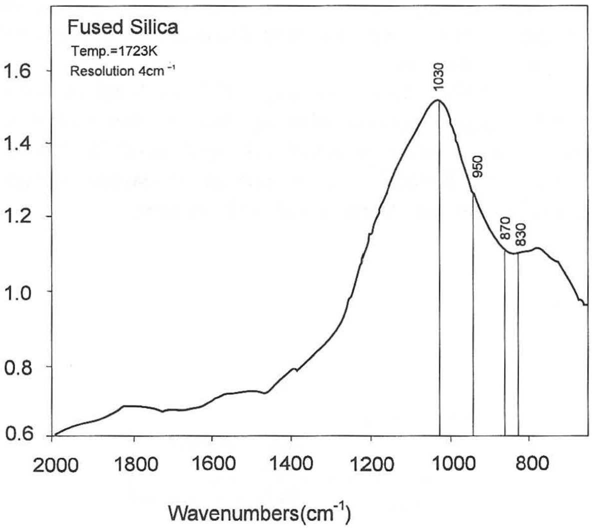

Figure 10 Emission spectra of fused silica at 1723K

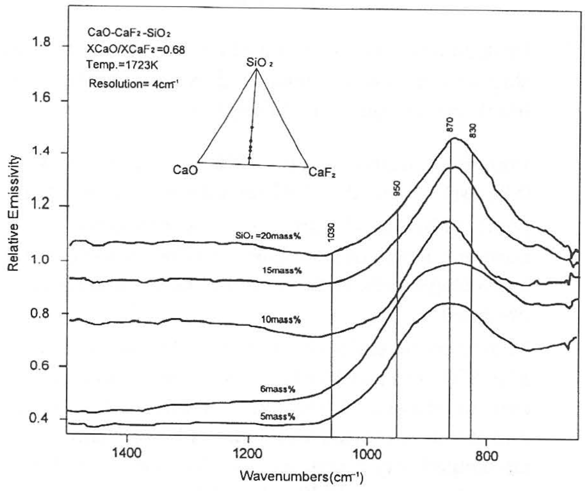

Figure 8 Emission spectra of molten slags with various silica content from 5 to 20 mass% at the ratio XCaO/XCaF$_2$=0.68

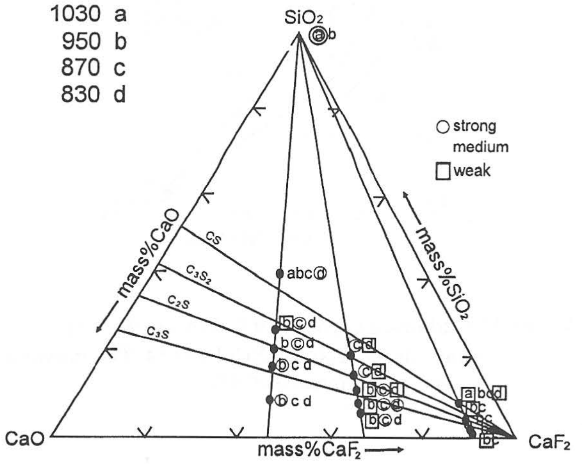

Figure 11 Intensity of characteristic emission at 1030, 950, 870 and 830 cm^{-1}

6. CARBONATE CAPACITY AND EMISSION SPECTRUM

Since carbonate capacity of slags in this area show an irregularity as reported by authors in previous papers, as in Figures 12 to 14, the carbonate capacity has the maximum at composition of $XCaO/XCaF_2$=0.14 and mass% of SiO_2 as 0.8.

Carbonate may dissolve in the molten slag as

$$CO_2 + O^{2-} = CO_3^{2-}$$

and carbonate capacity Cc is defined accordingly,

$$C_C = mass\%CO_3^{2-} / P_{CO_2}$$

Therefore higher the basicity higher the Cc may be expected. As in normal slag such as in CaO-SiO_2-Al_2O_3 or alkali silicate, a correlation between conventional refining capability and Cc agrees reasonably well. Beside the case of $XCaO/XCaF_2$=0.14, even at the present system, an increase in silica content in slag decreased Cc as expected (Figure 13 and 14).

If there is an exchange of Si-F- bond to Si-O- bond in higher concentration of fluoride, this maximum explained. Emission of such bond should be at 765 cm^{-1} as reported by Kumar[17)]. In the present investigation those emission was not clearly found in the system.

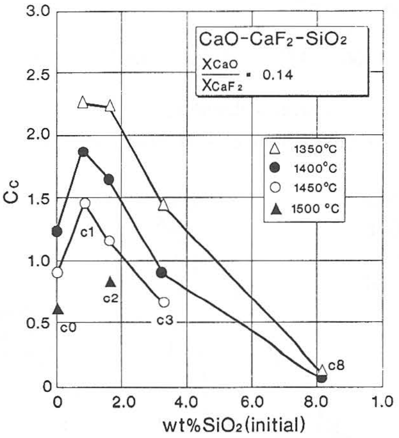

Figure 12 Carbonate capacity of CaO-CaF_2-SiO_2 at composition of $XCaO/XCaF_2$=0.14. The maximum is seen at 0.8 mass% of SiO_2.

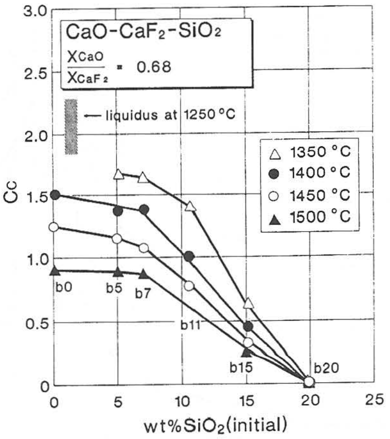

Figure 13 Carbonate capacity of CaO-CaF_2-SiO_2 at composition of $XCaO/XCaF_2$=0.68

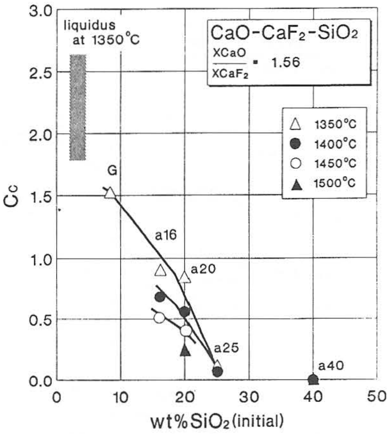

Figure 14 Carbonate capacity of CaO-CaF_2-SiO_2 at composition of $XCaO/XCaF_2$=1.56

7. CONCLUSION

1. Infrared emission spectrum of molten CaO-CaF_2-SiO_2 slag was successfully measured by a combination of hot thermocouple and FTIR system.

2. Emission spectrum of slag of $XCaO/XCaF_2$=0.14, 0.8mass% SiO_2, at 1473K resembles peaks at similar points (950 and 870 cm^{-1}) as for quenched slag, however, it was more vague at 1473K. A molten slag had a single peak at 890 cm^{-1} and no other clear peak observed.

3. Characteristic emission of molten slag was found at 830, 870, 950 and 1030 cm^{-1}. With increasing silica content emission at 830 and 1030 increased however, that at 950 decreased while that of 870 remain unchanged very much. At CaO/SiO_2 ratio less than unity, emission at 1030 is found that is attributable to SiO_4 tetrahedron.

4. No clear Si-F- bond was observed and irregularity of carbonate capacity at $XCaO/XCaF_2=0.14$ composition is remained unexplained.

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