

Structural Investigation of CaO–Al₂O₃ and CaO–Al₂O₃–CaF₂ Slags via Fourier Transform Infrared Spectra

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The FT-IR spectra of the CaO–Al₂O₃ and CaO–Al₂O₃–CaF₂ slags were measured to understand the structural aspects of (fluoro-) aluminate slags. The infrared spectra of the CaO–Al₂O₃ slag was interpreted based on the relationship between bond length and force constant of Al–O bond. Thereafter, the role of F[−] ions in the depolymerization of aluminate network was discussed. The wavenumbers of [AlO₄]-tetrahedra higher than that of [AlO₆]-octahedra would be originated from the Al–O bond length in tetrahedra shorter than that in octahedra. In the CaO_{satd}–Al₂O₃–CaF₂ system, the IR-transmitting bands of [AlO_nF_{4−n}]-complexes are observed through the entire composition of the fluoroaluminate system, while the bands of [AlO₄]-tetrahedra, [AlO₆]- and [AlF₆]-octahedra appear in the composition less than 24.0 (mol%) CaF₂. In the 26.2 (mol%) Al₂O₃-containing system, the bands of interlinked [AlO₄]-tetrahedra are shown at only 2-liquids boundary, while these bands are shown in the whole composition region in the 41.5 (mol%) Al₂O₃-containing system. In the 41.7 and 51.0 (mol%) CaO–Al₂O₃–CaF₂ systems, the transmitting bands of [AlO_nF_{4−n}]-complexes are observed through the entire composition, while those of [AlO₄]-tetrahedra are shown in the composition of $X_{CaF_2}/X_{Al_2O_3} \leq 1.0$. Also, the relative intensity of the bands indicating [AlO₄]-tetrahedra in the 51.0 (mol%) CaO-containing slag is much less than that in the 41.7 (mol%) CaO-containing system.

KEY WORDS: FT-IR spectra; bond length; force constant; depolymerization; [AlO₄]-tetrahedra; [AlO₆]-octahedra; [AlO_nF_{4−n}]-complexes.

1. Introduction

Because the CaO–Al₂O₃ and CaO–Al₂O₃–CaF₂ slags are basic systems in the secondary refining processes, various physicochemical properties of these slags have been studied.^{1–4)} However, although the slag properties are affected by its structure, the structural aspects of these slags have not fully been understood.

The structural aspects of aluminate systems have been reported by some scientists. Tarte proposed the characteristic frequency ranges for [AlO₄]-tetrahedra as 900–650 cm^{−1} and for [AlO₆]-octahedra as 680–400 cm^{−1} from the infrared spectra of inorganic calcium aluminates.⁵⁾ McMillan *et al.* interpreted the Raman spectrum of the 50 (mol%) CaO–Al₂O₃ system in terms of a fully polymerized network, which was depolymerized into the tetrahedral units with non-bridging oxygen (NBO)=1 and 2 on addition of CaO.⁶⁾ They also proposed that both Al coordination number (CN) and degree of polymerization within a fixed CN could affect the average ²⁷Al MAS-NMR spectra in the calcium aluminates.⁷⁾

On the other hand, Leekes *et al.* suggested that the asymmetric stretching vibration of the [AlO₄]-tetrahedra could be identified as an absorption band at 850–790 cm^{−1} from FT-IR spectra of the (fluoro-) calcium aluminate slags.⁸⁾ In the CaO–Al₂O₃–CaF₂ slag, the range of the F–Al–O vibra-

tions was nearly identical with that of Al–O vibrations; thus, Al³⁺ ions were considered to be tetrahedrally coordinated with oxygen and fluorine ions. They also discussed the relationship between CN and Al–O bond length on the basis of Badger's rule defined by Eq. (1).^{9–13)}

$$k^{-1/3} = a_{ij}(D_e - b_{ij}) \dots \dots \dots (1)$$

$$\nu = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}} \quad \text{or} \quad \tilde{\nu} = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}} \dots \dots \dots (2)$$

where k is the force constant for the vibration, D_e is the equilibrium bond length, a_{ij} and b_{ij} are constants determined by the nature of the bonded atoms. Also, ν , $\tilde{\nu}$, μ and c are, respectively, the frequency, wavenumber, reduced mass ($=m_1 \cdot m_2 / (m_1 + m_2)$, m_1 and m_2 are the masses of the two nuclei in a diatomic molecules or ions) and the velocity of light (3×10^8 m/sec). Equation (2) indicates that the wavenumber of specific vibration is in proportion to $k^{1/2}$ at a fixed μ . However, because slag composition they studied was significantly limited, more investigation through wide composition would be required.

For brevity, current studies indicate that the structure of quenched aluminate slags and glasses is similar to that of melts, because the glassy state is a supercooled liquid from the thermodynamic viewpoint. Regardless of various exper-

imental techniques, the common conclusions are that the aluminate structure would be composed of predominant $[\text{AlO}_4]$ -tetrahedron and minor $[\text{AlO}_6]$ -octahedron units. The shift of measured functions, for example FT-IR, Raman, and NMR spectra with slag composition would be associated with the change of Al–O bond length. Although the structural aspects of the CaO– Al_2O_3 slag have been reported, the role of CaF_2 in the depolymerization of aluminate network is not fully understood.

Therefore, in the present study, the FT-IR spectra of the CaO– Al_2O_3 slag was interpreted based on the relationship between bond length and force constant of Al–O bond. Thereafter, the role of F^- ions in the depolymerization of aluminate network was discussed in the viewpoint of physical properties of the CaO– Al_2O_3 – CaF_2 slag based on an analysis of FT-IR spectra.

2. Experimental

2.1. Specimen Preparation

Reagent-grade Al_2O_3 , CaF_2 and CaO calcined from reagent-grade CaCO_3 were mixed and melted in a graphite crucible under CO atmosphere during 64 800 sec at 1 823 and 1 773 K for the CaO– Al_2O_3 binary and CaO– Al_2O_3 – CaF_2 ternary slags, respectively, then water quenched. The almost samples were confirmed as a glassy type. In the case of CaO saturation condition, the crystallized parts were removed before conducting FT-IR spectra analysis. The contents of each component were determined by conventional titration methods and listed in Table 1.

2.2. Infrared Spectra Measurements

The structure of the investigated slags was analyzed by FT-IR spectroscopy (JASCO, FT/IR-300E). FT-IR transmitting spectra were recorded in the $4\,000$ – 400 cm^{-1} range using a spectrometer, equipped with a KBr (deuterated triglycine sulfate with potassium bromide windows) detector. A spectral resolution of 4 cm^{-1} was chosen. Each sample of 2.0 mg was mixed with 200 mg of KBr in an agate mortar, and then pressed into pellets of 13 mm diameter. The spectrum for each sample represents an average of 20 scans, which were normalized to the spectrum of the blank KBr pellet. The FT-IR spectra have been analyzed by computer software.

3. Results and Discussion

3.1. FT-IR Spectra of CaO– Al_2O_3 Slags

The IR-transmittance of the CaO– Al_2O_3 binary slags is shown in Fig. 1 as a function of wavenumber at different CaO contents. The three kinds of band groups are observed at about 960 – 600 cm^{-1} , 570 – 520 cm^{-1} , and 440 – 420 cm^{-1} ; these groups correspond to the asymmetric stretching vibration of $[\text{AlO}_4]$ -tetrahedra, $[\text{AlO}_6]$ -octahedra, and to the deformation of tetrahedra and octahedra units, respectively.^{5–9,14–17} Changes of the $[\text{AlO}_4]$ -tetrahedra bands with CaO content are very similar to the results reported by Leekes *et al.*, who measured the infrared spectra of molten CaO– Al_2O_3 slags at 1 873 K.⁸

The transmitting bands for $[\text{AlO}_4]$ -tetrahedra at 690 and 630 cm^{-1} in the CaO· Al_2O_3 saturated composition shift to

Table 1. Experimental compositions for the IR spectra analysis.

No.	CaO (mol%)	Al_2O_3 (mol%)	CaF_2 (mol%)
1-1	56.7	43.3	0.0
1-2	60.6	39.4	0.0
1-3	64.1	35.9	0.0
1-4	68.4	31.6	0.0
1-5	71.1	28.9	0.0
2-1	72.1	26.8	1.1
2-2	67.7	22.7	9.6
2-3	65.8	20.1	14.1
2-4	60.7	15.3	24.0
2-5	50.4	13.1	36.5
2-6	39.7	4.7	55.6
2-7	32.1	0.0	67.9
2-8	59.9	26.4	13.7
2-9	50.8	34.8	14.4
2-10	44.5	40.7	14.8
2-11	30.6	42.6	26.8
2-12	41.3	40.8	17.9
2-13	43.4	29.6	27.0
2-14	44.3	25.4	30.3
2-15	51.7	24.8	23.5
2-16	35.4	27.0	37.6

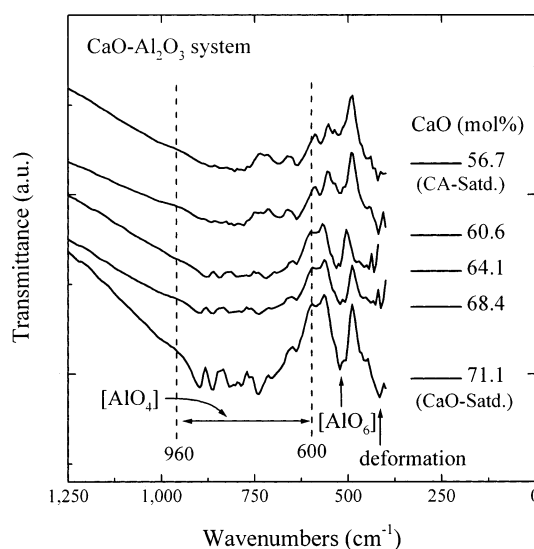


Fig. 1. IR-transmittance of the CaO– Al_2O_3 slag as a function of wavenumbers at different compositions.

720 and 640 cm^{-1} , respectively in the composition higher than 64.1 (mol%) CaO. These bands gradually merged into weak shoulder of broad and strong one, of which center of gravity is at about 780 cm^{-1} . Also, this strong and broad band continuously splits up with increasing CaO content to the CaO saturated composition.

On the other hand, there are no shifts for the transmitting bands of $[\text{AlO}_6]$ -octahedra and deformation bands, which would be less sensitive to the structural changes than $[\text{AlO}_4]$ -tetrahedra would be.^{8,9} However, the relative intensity of $[\text{AlO}_6]$ -octahedra continuously increases with increasing CaO content, indicating that the oxygen ions dissociated from CaO would react with $[\text{AlO}_4]$ -tetrahedra to produce $[\text{AlO}_6]$ -octahedra, based on Eq. (3).

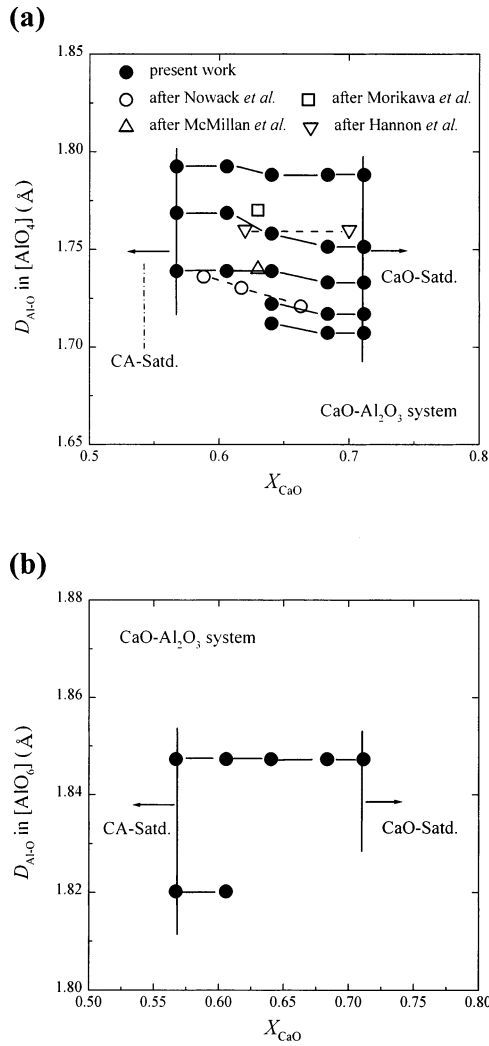


Fig. 2. Bond length between Al and O atoms (a) in the [AlO₄]-tetrahedra and (b) in the [AlO₆]-octahedra units.

$$n[\text{AlO}_4]^{5-} + 2n\text{O}^{2-} = n[\text{AlO}_6]^{9-} \dots\dots\dots(3)$$

McMillan and Piriou suggested that continuous addition of CaO into the aluminates would result in an unstable network of depolymerized tetrahedral aluminate groups, which distort with acceptance of slightly higher average coordination unit such as octahedra to accommodate the excess oxygen.⁶⁾

Current studies in the literature have indicated that the shift of spectroscopic (FT-IR and Raman) bands of a network formation unit with increasing content of network modifier would be originated from the change of bond length between two atoms such as Al-O bond.^{5-8,14)} Figure 2 exhibits the Al-O bond length in the (a) [AlO₄]-tetrahedra and (b) [AlO₆]-octahedra calculated from the Badger's rule (Eq. (1)) as a function of slag composition. The constants in Eq. (1), *a_{ij}* and *b_{ij}* are given for the type of chemical bonds.¹¹⁾ In the case of Al-O bond, the values of *a_{Al-O}* and *b_{Al-O}* have been taken to be 1.87 and 0.94 Å, respectively. In Fig. 2(a), the Al-O bond length is about 1.74–1.79 Å at the CaO·Al₂O₃ saturated condition and changes with CaO addition. Finally, the Al-O bond length in the [AlO₄]-tetrahedra at CaO saturated composition is fixed to approximately two groups; one is 1.79 Å, and the other is the range of

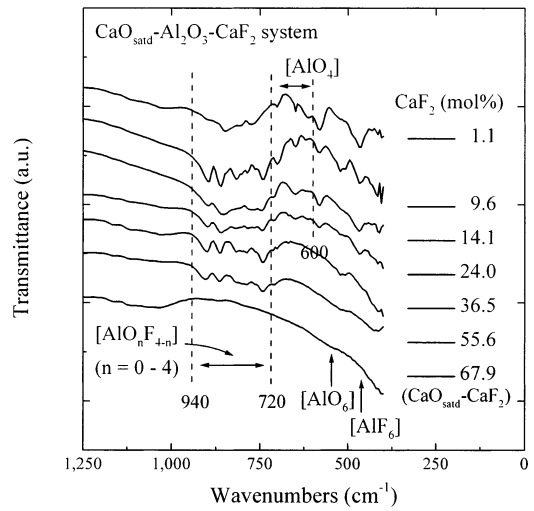


Fig. 3. IR-transmittance of the CaO_{satd}-Al₂O₃-CaF₂ system at different CaF₂ contents.

1.75–1.71 Å with an average value of 1.73 Å. The values reported by other researchers are within the range of 1.72–1.77 Å.^{7,8,18,19)} The split of Al-O bond length would result from the changes in the degree of polymerization of [AlO₄]-tetrahedra with increasing CaO content.⁸⁾

On the other hand, the Al-O bond length in the [AlO₆]-octahedra unit is nearly constant as about 1.85 and 1.82 Å (Fig. 2(b)) by increasing the content of CaO. Therefore, it can be suggested that the wavenumbers of [AlO₄]-tetrahedra higher than that of [AlO₆]-octahedra would be originated from the Al-O bond length in tetrahedra shorter than that in octahedra. It is also proposed that the physical properties of aluminates would be dependent on the distribution of [AlO₄]-tetrahedra and [AlO₆]-octahedra units in slags.

3.2. Structural Aspects of CaO-Al₂O₃-CaF₂ Slags

In fluoride-containing slags, the F⁻ ions as well as O²⁻ ions play an important role in the depolymerization of network structure. In Sec. 3.1., the role of O²⁻ ions without F⁻ ions in the depolymerization reaction of aluminate network was discussed. From these backgrounds, the effect of F⁻ ions on aluminate structure will be discussed.

3.2.1. Effect of F⁻ Addition at CaO Saturation Condition

Figure 3 exhibits the IR-transmittance of the CaO_{satd}-Al₂O₃-CaF₂ system as a function of wavenumber at different CaF₂ contents. There are four kinds of band groups at about 940–720, 720–600, 580 and 470 cm⁻¹; these groups, respectively, correspond to the asymmetric stretching vibration of the [AlO_nF_{4-n}] (*n*=0–4) tetrahedral complexes, [AlO₄]-tetrahedra, [AlO₆]-octahedra, and [AlF₆]-octahedra.^{5-9,14-17)} The assignment of band groups at about 940–720 cm⁻¹ to the [AlO_nF_{4-n}]-complexes is based on an increased asymmetry of vibration due to coexistence of Al-F and Al-O bonds in these complexes.⁸⁾

The transmitting bands of [AlO_nF_{4-n}]-complexes are shown through the entire composition of the fluoroaluminate system, while the bands of [AlO₄]-tetrahedra, [AlO₆]- and [AlF₆]-octahedra appear in the composition less than 24.0 (mol%) CaF₂. Based on these experimental results, the following depolymerization reaction of aluminate network by F⁻ ions could be proposed at less than 24.0 (mol%) CaF₂:

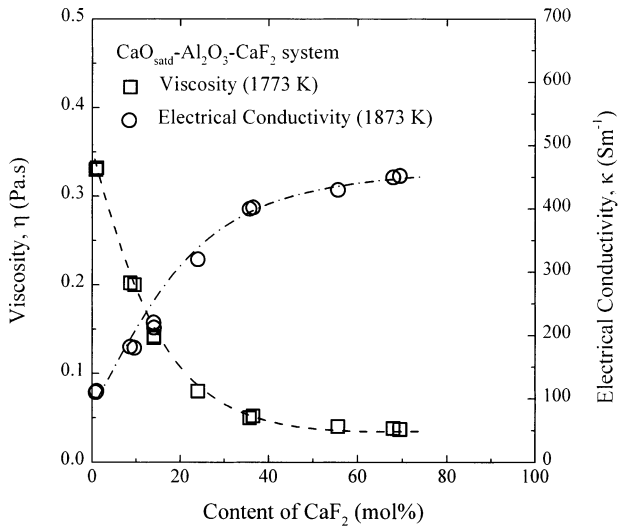
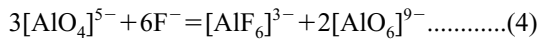


Fig. 4. Physical properties of the CaO_{satd}-Al₂O₃-CaF₂ system available in the literature as a function of CaF₂ content.



Equation (4) indicates that the product of activities of aluminate tetrahedra and F⁻ ions could be a driving force for the depolymerization of aluminate network by F⁻ ions under the condition of *a*_{CaO} = 1.

However, in the composition at *X*_{CaF₂} ≥ 0.24, because the activity of Al₂O₃ is significantly low (*a*_{Al₂O₃} ≤ 4 × 10⁻⁴ at 1773 K) and, at the same time, the activity of CaF₂ is nearly constant with CaF₂ content, the driving force of the reaction given in Eq. (4) would be less than the activation energy.¹⁾ Consequently, the depolymerization reaction of aluminate network by F⁻ ions would be limited, and the residual Al³⁺ ions would simultaneously be coordinated with oxygen and fluorine ions, resulting in the formation of [AlO_{*n*}F_{4-*n*}]-complexes.^{8,9)}

Figure 4 exhibits the viscosity and electrical conductivity of the CaO_{satd}-Al₂O₃-CaF₂ system at 1773 and 1873 K, respectively, as functions of CaF₂ content.⁴⁾ Viscosity and electrical conductivity of slags sharply decreases and increases with increasing CaF₂ content up to about 25 mol%, respectively, followed by nearly constant value of 0.04–0.05 Pa·s and of 400–450 S m⁻¹.

The physical properties of molten slags have been known to depend on melt structure, which would dominantly be affected by the degree of polymerization.^{20,21)} Thus, the significant variation of physical properties of slags at a fixed chemical potential of CaO is mainly attributed to the depolymerization of aluminate network by addition of F⁻ ions up to about *X*_{CaF₂} ≈ 0.25. Therefore, it is qualitatively suggested that the depolymerization reaction by F⁻ ions would be limited at higher CaF₂ content region (≥ 25 mol%). These macroscopic phenomena such as viscosity could be understood on the basis of microscopic structural aspects with an analysis of FT-IR spectra as discussed above.

3.2.2. Effect of Slag Composition on Fluoroaluminate Structure

Figure 5 exhibits the IR-transmittance of the (a) CaO–26.2(mol%)Al₂O₃-CaF₂ and (b) CaO–41.5(mol%)Al₂O₃-CaF₂ systems as a function of wavenumber at differ-

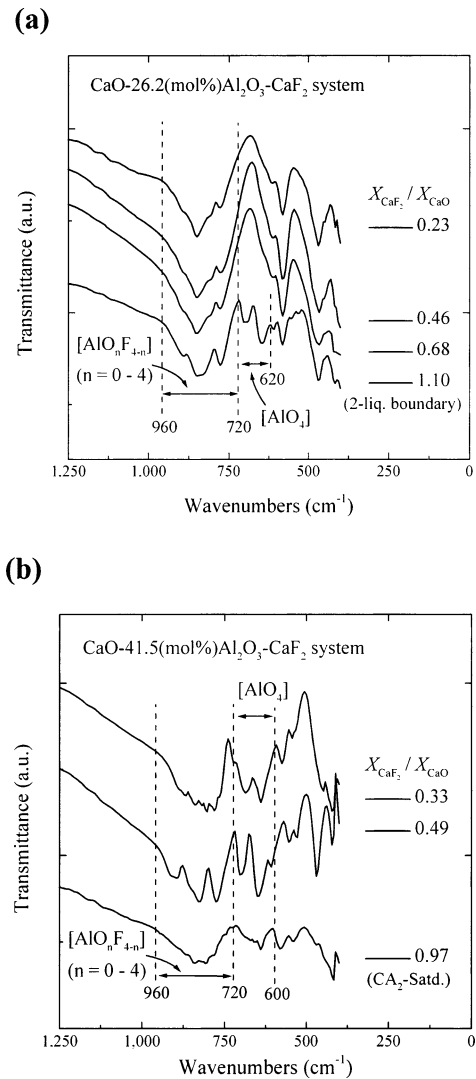


Fig. 5. IR-transmittance of the (a) CaO–26.2(mol%)Al₂O₃-CaF₂ and (b) CaO–41.5(mol%)Al₂O₃-CaF₂ systems at different CaF₂/CaO ratios.

ent ratio of CaF₂ to CaO on a molar basis. In the 26.2 (mol%) Al₂O₃-containing system, the bands of [AlO₄]-tetrahedra are observed at only 2-liquids boundary, while these bands are shown in the whole composition region in the 41.5 (mol%) Al₂O₃-containing system.

As shown in Fig. 5(a), the [AlO₄]-tetrahedra bands are only observed at 2-liquids boundary, indicating that this composition is close to the Al₂O₃-rich phase. Hence, the role of F⁻ ions in the modification of aluminate network of the 26.2 (mol%) Al₂O₃-containing system would be limited. Also, the bands of [AlO_{*n*}F_{4-*n*}]-complexes are not seriously changed with slag composition, indicating that the degree of polymerization of [AlO_{*n*}F_{4-*n*}]-complexes would not be affected by composition.

However, the bands of [AlO₄]-tetrahedra are observed through the entire homogeneous liquid phase at high Al₂O₃-containing system (Fig. 5(b)); this means that the F⁻ ions enhance the depolymerization reaction such as Eq. (4). Hence, the modification of aluminate network by F⁻ ions would be effective under condition that slag network is composed of tetrahedra, that is, major structure formation units.

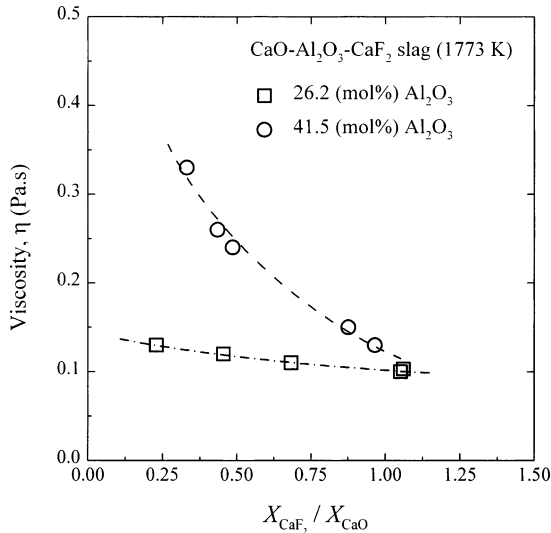


Fig. 6. Viscosities of the CaO–26.2(mol%)Al₂O₃–CaF₂ and CaO–41.5(mol%)Al₂O₃–CaF₂ systems available in the literature as a function of ratio CaF₂/CaO.

The viscosity of the CaO–26.2(mol%)Al₂O₃–CaF₂ and CaO–41.5(mol%)Al₂O₃–CaF₂ systems at 1773 K is shown in **Fig. 6** as a function of $X_{\text{CaF}_2}/X_{\text{CaO}}$ (F/C) ratio.⁴⁾ The viscosity of the 26.2 (mol%) Al₂O₃-containing system is nearly constant as about 0.1 Pa·s in homogeneous liquid phase, while that of the 41.5 (mol%) Al₂O₃-containing system significantly decreases with increasing F/C ratio from 0.3 to 1.0. These trends indicate that the substitution of F[−] for O^{2−} ions would have no significant effect on structure modification in the relatively low-Al₂O₃ melt; however, the substitution has dominant effect on the modification of aluminate network in the relatively high-Al₂O₃ system.

Figure 7 exhibits the IR-transmittance of the (a) 41.7(mol%)CaO–Al₂O₃–CaF₂ and (b) 51.0(mol%)CaO–Al₂O₃–CaF₂ systems as a function of wavenumber at different $X_{\text{CaF}_2}/X_{\text{Al}_2\text{O}_3}$ (F/A) ratios. The transmitting bands of [AlO_nF_{4−n}]-complexes are observed through the entire composition, while those of [AlO₄]-tetrahedra are shown in the composition of F/A ≤ 1.0. The relative intensity of the bands indicating [AlO₄]-tetrahedra in **Fig. 7(b)** is much less than that in **Fig. 7(a)**; it means that the more the content of CaO, the stronger the potential of O^{2−} ions contributing to the depolymerization reaction.

In both of the slags, the transmitting bands of [AlO₄]-tetrahedra disappear and merged into the bands of [AlO_nF_{4−n}]-complexes with increasing F/A ratio. Therefore, the depolymerization of aluminate network by F[−] ions would occur within the composition limit up to about F/A ≅ 1.0. In the composition region higher than F/A ≅ 1.0, slag network is probably composed of the partially depolymerized [AlO_nF_{4−n}]-complexes.

The viscosity of the 41.7 and 51.0(mol%)CaO–Al₂O₃–CaF₂ systems at 1773 K is shown in **Fig. 8** as a function of F/A ratio.⁴⁾ Viscosity of slags significantly decreases with increasing F/A ratio up to about unity, followed by slight decrease less than 0.1 Pa·s. Therefore, it is qualitatively suggested that the depolymerization reaction by F[−] ions would be significant in the composition of F/A ≤ 1.0, while F[−] effect on network modification would be limited at the ratio of CaF₂ to Al₂O₃ higher than unity as discussed above.

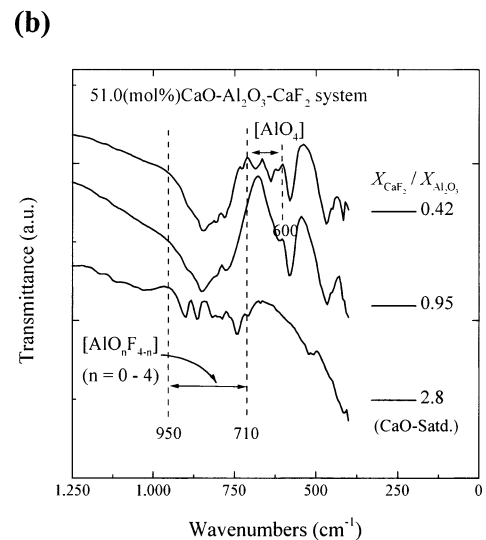
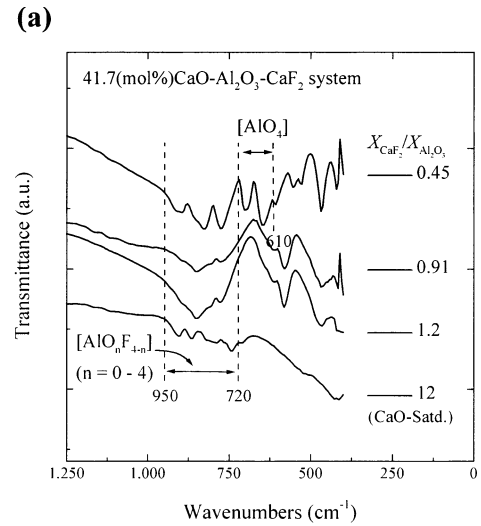


Fig. 7. IR-transmittance of the (a) 41.7(mol%)CaO–Al₂O₃–CaF₂ and (b) 51.0(mol%)CaO–Al₂O₃–CaF₂ systems at different CaF₂/Al₂O₃ ratios.

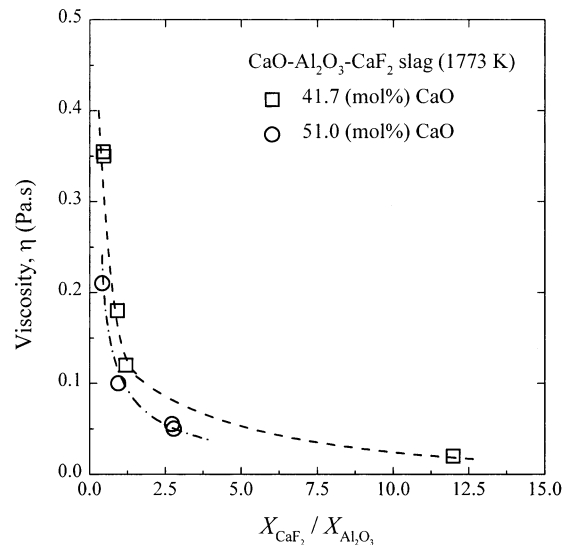


Fig. 8. Viscosities of the 41.7 and 51.0(mol%)CaO–Al₂O₃–CaF₂ systems available in the literature as a function of ratio CaF₂/Al₂O₃.

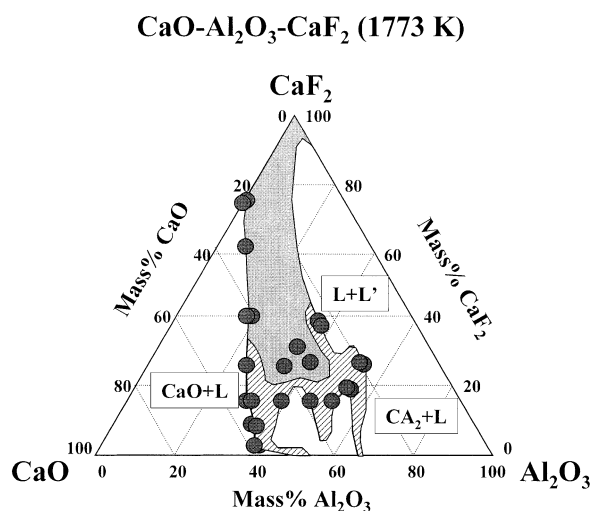


Fig. 9. Existence area of $[\text{AlO}_4]$ -tetrahedra units in the $\text{CaO}-\text{Al}_2\text{O}_3-\text{CaF}_2$ slag at 1773 K from the FT-IR spectra analysis.

3.2.3. Summary

Figure 9 exhibits the equilibrium phase diagram of the $\text{CaO}-\text{Al}_2\text{O}_3-\text{CaF}_2$ slag at 1773 K with experimental compositions marked as solid circles.²²⁾ The hatched area indicates the existence of $[\text{AlO}_4]$ -tetrahedra from FT-IR spectra; thus the depolymerization of aluminate network by F^- as well as O^{2-} ions would be available. Actually, the viscosity and electrical conductivity of slags slightly change with increasing CaF_2 content in non-hatched composition; however, this change of slag properties would be due to slight decrease in the degree of polymerization of $[\text{AlO}_n\text{F}_{4-n}]$ -complexes by O^{2-} ions. Figure 9 may give useful information regarding the input limit of CaF_2 into the aluminate slags to increase the fluidity in the secondary refining processes and conductivity in the electro slag remelting (ESR) processes, etc.

4. Conclusions

The FT-IR spectra of the $\text{CaO}-\text{Al}_2\text{O}_3$ and $\text{CaO}-\text{Al}_2\text{O}_3-\text{CaF}_2$ slags were measured to understand the structural aspects of (fluoro-) aluminate slags. The infrared spectra of the $\text{CaO}-\text{Al}_2\text{O}_3$ slag were interpreted based on the relationship between bond length and force constant of Al-O bond. Thereafter, the role of F^- ions in the depolymerization of aluminate network was discussed. The following conclusions could be obtained:

(1) The wavenumbers of $[\text{AlO}_4]$ -tetrahedra higher than that of $[\text{AlO}_6]$ -octahedra would be originated from the Al-O bond length in tetrahedra shorter than that in octahedra.

(2) In the $\text{CaO}_{\text{satd}}-\text{Al}_2\text{O}_3-\text{CaF}_2$ system, the IR-transmitting bands of $[\text{AlO}_n\text{F}_{4-n}]$ -complexes are observed through the entire composition of the fluoroaluminate system, while the bands of $[\text{AlO}_4]$ -tetrahedra, $[\text{AlO}_6]$ - and $[\text{AlF}_6]$ -octa-

dra appear in the composition less than 24.0 (mol%) CaF_2 .

(3) In the $\text{CaO}-26.2(\text{mol}\%)\text{Al}_2\text{O}_3-\text{CaF}_2$ system, the bands of $[\text{AlO}_4]$ -tetrahedra are shown at only 2-liquids boundary, while these bands are shown in the whole composition region in the $\text{CaO}-41.5(\text{mol}\%)\text{Al}_2\text{O}_3-\text{CaF}_2$ system.

(4) In the 41.7 and 51.0 (mol%) $\text{CaO}-\text{Al}_2\text{O}_3-\text{CaF}_2$ systems, the transmitting bands of $[\text{AlO}_n\text{F}_{4-n}]$ -complexes are observed through the entire composition, while those of $[\text{AlO}_4]$ -tetrahedra are shown in the composition of $X_{\text{CaF}_2}/X_{\text{Al}_2\text{O}_3} \leq 1.0$. Also, the relative intensity of the bands indicating $[\text{AlO}_4]$ -tetrahedra in 51.0 (mol%) CaO -containing slag is much less than that in the 41.7 (mol%) CaO -containing system.

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REFERENCES

- 1) M. Hino, S. I. Kinoshita, Y. Ehara, H. Itoh and S. Ban-ya: Proc. 5th Int. Conf. Molten Slags, Fluxes and Salts, ISS-AIME, Warrendale, PA, (1997), 53.
- 2) G. J. W. Kor and F. D. Richardson: *Trans. TMS-AIME*, **245** (1969), 319.
- 3) I. Sohn, D. J. Min and J. H. Park: *Steel Res.*, **70** (1999), 215.
- 4) K. C. Mills: Slag Atlas, 2nd ed., Verlag Stahleisen GmbH, Düsseldorf, (1995), 362, 567.
- 5) P. Tarte: *Spectrochim. Acta*, **23A** (1967), 2127.
- 6) P. McMillan and B. Piriou: *J. Non-Cryst. Solids*, **55** (1983), 221.
- 7) P. F. McMillan, W. T. Petuskey, B. Coté, D. Massiot, C. Landron and J. P. Coutures: *J. Non-Cryst. Solids*, **195** (1996), 261.
- 8) G. Leekes, N. Nowack and F. Schlegelmilch: *Steel Res.*, **59** (1988), 406.
- 9) K. Mausbach, N. Nowack and F. Schlegelmilch: *Steel Res.*, **64** (1993), 239.
- 10) R. M. Badger: *J. Chem. Phys.*, **3** (1935), 710.
- 11) L. Pauling: The Nature of the Chemical Bond, 3rd ed., Cornell University Press, New York, (1960), 231.
- 12) K. Nakamoto: Infrared and Raman Spectra of Inorganic and Coordination Compounds, 5th ed., Part A, John Wiley & Sons, New York, (1997), 10.
- 13) C. J. H. Schutte: The Theory of Molecular Spectroscopy, Vol. I, North Holland, Amsterdam, (1976).
- 14) R. A. Schroeder and L. L. Lyons: *J. Inorg. Nucl. Chem.*, **28** (1966), 1155.
- 15) A. Aronne, S. Esposito and P. Pernice: *Mater. Chem. Phys.*, **51** (1997), 163.
- 16) L. Stoch and M. Sroda: *J. Mol. Struct.*, **511-512** (1999), 77.
- 17) P. Pernice, S. Esposito, A. Aronne and V. N. Sigaev: *J. Non-Cryst. Solids*, **258** (1999), 1.
- 18) H. Morikawa, F. Marumo, T. Koyama, M. Yamane and A. Oyobe: *J. Non-Cryst. Solids*, **56** (1983), 355.
- 19) A. C. Hannon and J. M. Parker: *J. Non-Cryst. Solids*, **274** (2000), 102.
- 20) K. C. Mills: *ISIJ Int.*, **33** (1993), 148.
- 21) K. C. Mills and S. Sridhar: *Ironmaking Steelmaking*, **26** (1999), 262.
- 22) M. Kowalski, P. J. Spencer and D. Neuschütz: Slag Atlas, 2nd ed., Verlag Stahleisen GmbH, Düsseldorf, (1995), 191.