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TECHNICAL REVIEW

Structure of Slag (Report VIII)†
− State of Three Sorts of Oxygens in Slag −

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Abstract

It is important to determine ionic fractions of three sorts of oxygens in slag from the standpoint to minimize the contents of sulphur and phosphor and invasion of water vapor in molten metal by using appropriate slag composition.

Until now, several means to obtain ionic fractions of three sorts of oxygens in slag were proposed. In this report, theoretical and experimental including molar refraction, Raman spectroscopy, ESCA and Trimethylsilyl derivative means are summarized.

KEY WORDS: (Slag) (State Analysis)

1. Introduction

A design to determine the appropriate slag composition has become more important for the following objects:
to minimize the contents of sulphur and phosphor
to prevent the invasion of hydrogen on welding in water
to lessen the contents of oxygen and nitrogen which give harmful action on toughness of weld metal.

Already the author have indicated the problems occuring in welding. In this review it is summerized that the three sorts of oxygen in slag, O^0, O^- and O^{2-}, has how effect on chemical reaction and the development to determine the quantities owes to what kinds of analysis.

## 2. Significance to know the state of oxygen in slag

Although steelmakers in Japan can obtain good quality of iron ore containing less phosphor, recently the concern has been aimed to produce higher quality of steel having less sulphur as well as phosphor by using additional treatment of external desulphurization combined with dephosphorization. Therefore a design to determine the appropriate composition of slag having superior characteristics for the chemical reaction between molten steel and slag has become more important.

As for desulphurization of molten metal, it is generally accepted the exhange reaction of electron[1] as following

$$\underline{S} + (O^{2-}) \rightarrow (S^{2-}) + \underline{O} \qquad (1)$$
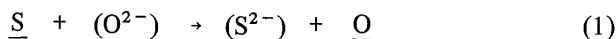
From this equation it is known the importance of free oxygen (O^{2-}) in slag for the desulphorization.
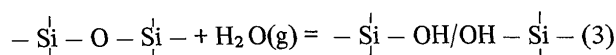
When simply considered, the following equation is given to proceed dephosphorization. Likewise it will be understood that free oxygen (O_2^{2-}) in slag is necessary for dephosphorization although the existence of oxygen in molten metal does take part which is basically different to desulphurization.
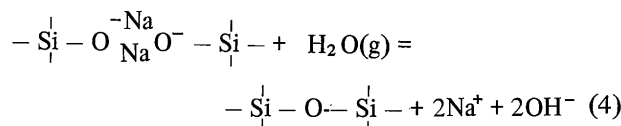
$$2P + 5\underline{O} + 3(Na_2O)' \rightarrow 3Na_2O \cdot P_2O_5 \qquad (2)$$
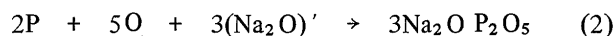
where $(Na_2O)'$ means free Na_2O in slag which does not combine with P_2O_5, SiO_2 and S.

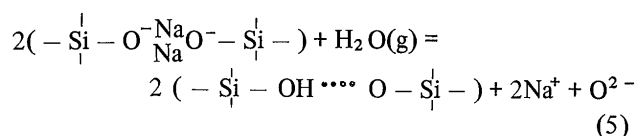In regards to solution of water vapor and the diffusion of hydrogen in slag, the following mechanisms are given[2][3].
In the acidic slag,

$$- \overset{|}{\underset{|}{Si}} - O - \overset{|}{\underset{|}{Si}} - + H_2O(g) = - \overset{|}{\underset{|}{Si}} - OH/OH - \overset{|}{\underset{|}{Si}} - \quad (3)$$

In the basic slag,

$$- \overset{|}{\underset{|}{Si}} - O \overset{-Na}{\underset{Na}{}} O^- - \overset{|}{\underset{|}{Si}} - + H_2O(g) =$$

$$- \overset{|}{\underset{|}{Si}} - O - \overset{|}{\underset{|}{Si}} - + 2Na^+ + 2OH^- \quad (4)$$

or [4]

$$2(- \overset{|}{\underset{|}{Si}} - O \overset{-Na}{\underset{Na}{}} O^- - \overset{|}{\underset{|}{Si}} -) + H_2O(g) =$$

$$2(- \overset{|}{\underset{|}{Si}} - OH \cdots O - \overset{|}{\underset{|}{Si}} -) + 2Na^+ + O^{2-} \quad (5)$$
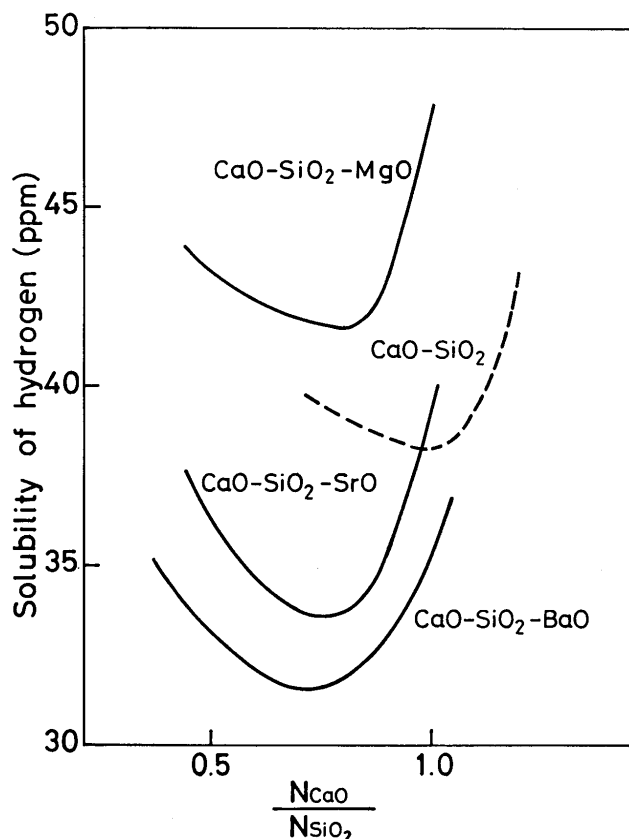
Fig.1 Solubility of hydrogen content in the CaO-SiO$_2$-alkaline earth metal oxide

2.1 Theoretical induction

Lin and Pelton introduced a structural model for binary silicate systems.[7] When MO and SiO$_2$ were mixed, the reaction expreesed in equation (7) occurs. Therefore molar enthalpy of mixing, ΔH, can be written as Toop and Samis.[8]
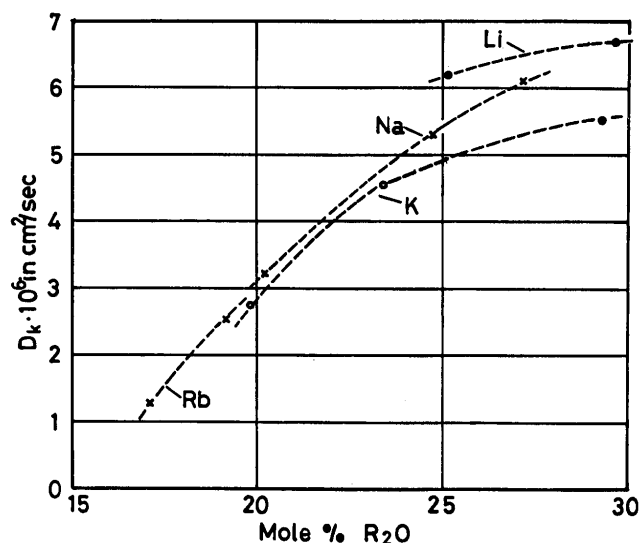

Fig.2 Relationship between the diffusion coefficient of water in a glass melt and alkali metal oxide content in alkalisilicate glass.
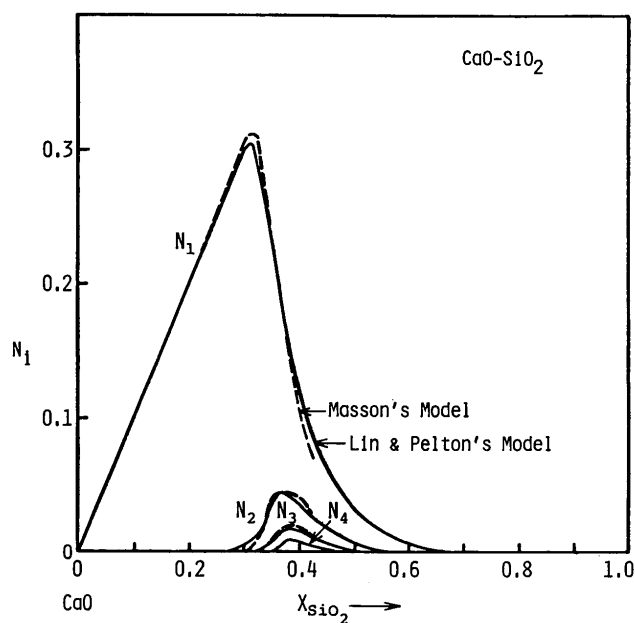
In the strong basic slag

$$O^{2-} + H_2O(g) = 2(OH^-) \tag{6}$$

From the relationship between solubility of water vapor and the content of basic oxide added in slag, it can be thought that O° and O^{2-} in slag plays an important role on solubility of water vapor respectively.[5]

The estimate can be explained from the result on solubility of water vapor (**Figure 1**) and the Figures which show comparison with fractions of three sorts of oxygen in slag and they are given afterwards.

Although the author can not consider the mechanism on diffusion of water in glass because the results are only given for the composition having basic oxide within the range 17 ~ 30 mole percentage as shown in **Figure 2**[6], half-bonded oxygen (O$^-$) in glass seems to play as important role on diffusion of water in glass. That is to say, OH$^-$ group formed according to equation (6) can transfer proton (H$^+$) to a neighboring halfbonded oxygen (O$^-$)by jumping mean.

Fig.3 Number of monomers (N$_1$), dimers (N$_2$), trimers (N$_3$), and tetramers (N$_4$) in the CaO-SiO$_2$ system at 1600°C.

$$O^{\circ} + O^{2-} \rightarrow 2O^{-} \tag{7}$$

$$\Delta H = N_0^-/2 \cdot \Delta e \tag{8}$$

Where Δe is the molar energy change for eq. (8).

They introduced parameters, A, B and C, to obtain good fits between experimentally determined integral molar enthalpies and calculated one.

$$\Delta H = (N_0^-/2)(A\,X_{MO} + B\,X_{SiO_2} + C\,X_{MO}\,X_{SiO_2})$$
$$= (N_0^-/2)\,\Delta e \tag{9}$$

Considering the reaction, eq (7), ΔH can be expressed as follows:

$$\Delta H = (N_{O^{2-}} \cdot e_O^{2-} + N_O^{\circ} e_O^{\circ} + N_O^- e_O^-)$$
$$- X_{MO}\, e_O^{2-}(MO) - 2X_{SiO_2}\, e_O^{\circ}(SiO_2) \tag{10}$$

where e_O^{2-}, e_O^- and e_O° are the molar energies of each oxygen species.

Under an approximation that e_O° is nearly constant for $X_{SiO_2} < 1/3$, eq.(10) can be reduced simply as

$$\Delta H = N_O^-/2\,(2e_O^- - e_O^{2-}(MO) - e_O^{\circ}(SiO_2)) \tag{11}$$

Further N_O^-, N_O^{2-} and N_O° could be calculated with the combination of equations (12) - (15).

$$- (A\,X_{MO} + BX_{SiO_2} + CX_{MO}\,X_{SiO_2})$$
$$+ RT[\ln(N_O^2/X_{SiO_2} + N_O^{2-}) + \ln(N_O^{\circ}/N_{Si-Si})$$
$$- (1 + N_{Si-Si}/X_{SiO_2} + N_O^{2-})\ln(N_{Si-Si} - N_O^{\circ}/N_{Si-Si})]$$
$$= 0 \tag{13}$$

The comparison with various polymeric species calculated by Masson[9] are given in **Figures (3) ~ (6)**. Remarkable difference can be found in which various polyanions can have definite value through $X_{SiO_2} = 1/2$.

On the other hand, Borgiani and Granati applied Montecarlo calculation to determine the structures of slag.[10] The results obtained are given in **Figures (7) ~ (10)**. From these diagrams, considerable differences on the fraction of different ionic species can be seen when the comparison with Figs. (3) ~ (6) was done.

We must say that great interest is focussed on the results when Al_2O_3 or FeO was added to slag of the system CaO-SiO_2. In the cases, it can be observed that the decrease of molar fraction of SiO_4^{4-} and the increase of complex chains has occured.
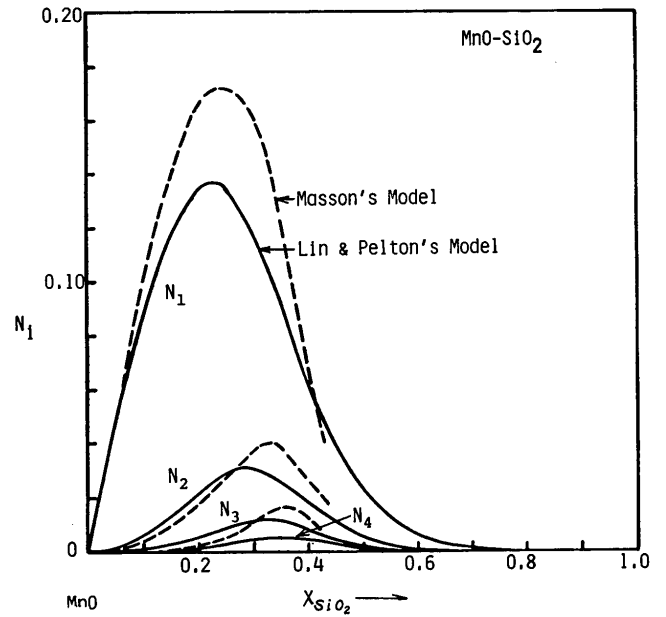

Fig.4 Number of monomers (N_1), dimers (N_2), trimers (N_3), and tetramers (N_4) in the MnO-SiO_2 system at $1600^{\circ}C$.
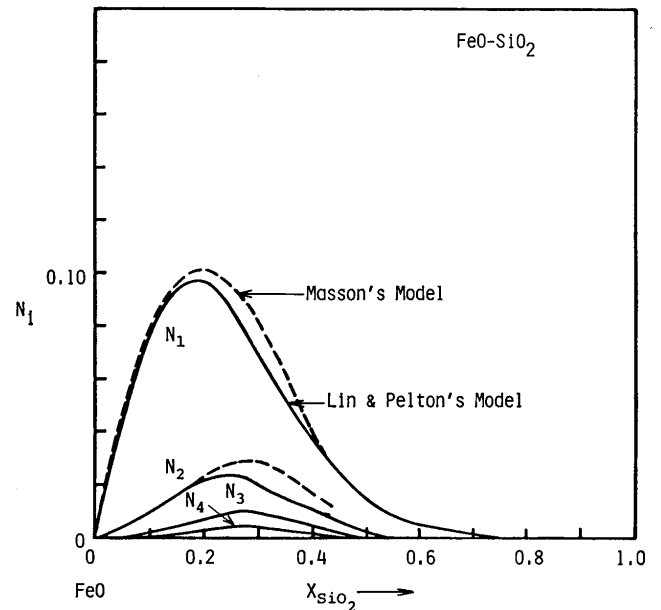

Fig.5 Number of monomers (N_1), dimers (N_2), trimers (N_3), and tetramers (N_4) in the FeO-SiO_2 system at $1600^{\circ}C$.

However as shown in **Figure (11) ~ (12)** obtained with Raman scattering study on the systems, Na_2O- and K_2O-SiO_2 - Al_2O_3 [11] it can be determined that the intensity of 980 cm^{-1} band increases while that of 1100 cm^{-1} band decreases with Al_2O_3 content. The authors suggested that the bands, 980 and 1100 cm^{-1} would arise from the SiO_4 tetrahedron with one or two non-bridging and four bridging oxygens respectively.

The contradiction must be resolved with the application of another physical means.
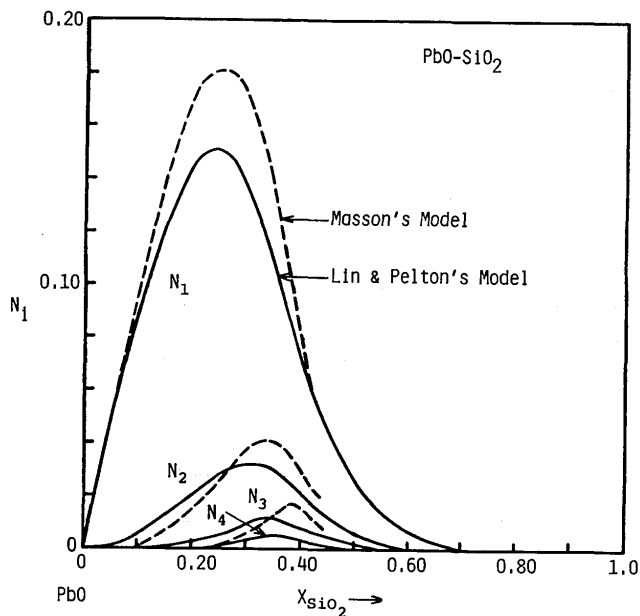

Fig.6 Number of monomers (N_1), dimers (N_2), trimers (N_3), and tetramers (N_4) in the system PbO-SiO$_2$ at $1000°$C.
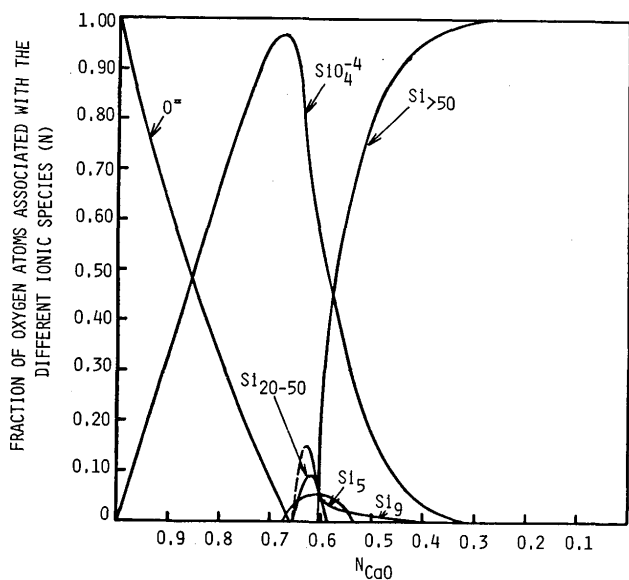

Fig.7 Fraction of the oxygen associated with the different ionic species for the system CaO-SiO$_2$
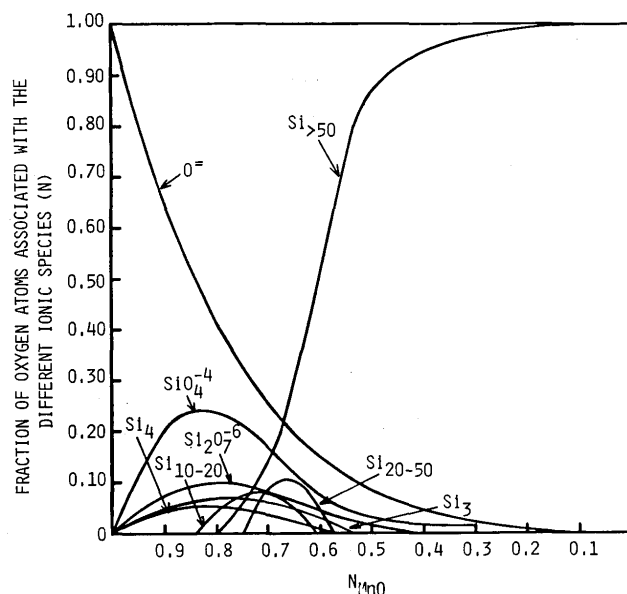

Fig.8 Fraction of the oxygen associated with the different ionic species for the system MnO-SiO$_2$

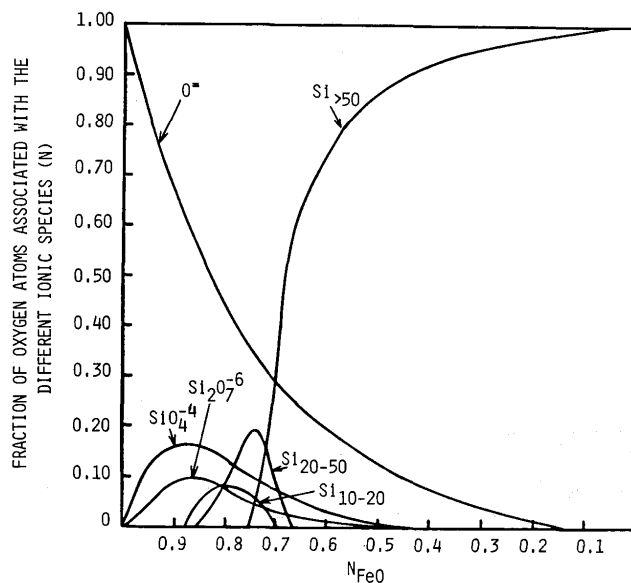**Fig.9** Fraction of the oxygen associated with the different ionic species for the system FeO-SiO$_2$

2.2 Experimental induction

2.2.1 Molar refractivity[12]

It is well known that the ionic refractivity can be related to the ionic radius and a highly charged, small cation scarcely contributes to the molar refractivity.

Ionic fractures of three sorts of oxygens were calculated under the following assumptions:
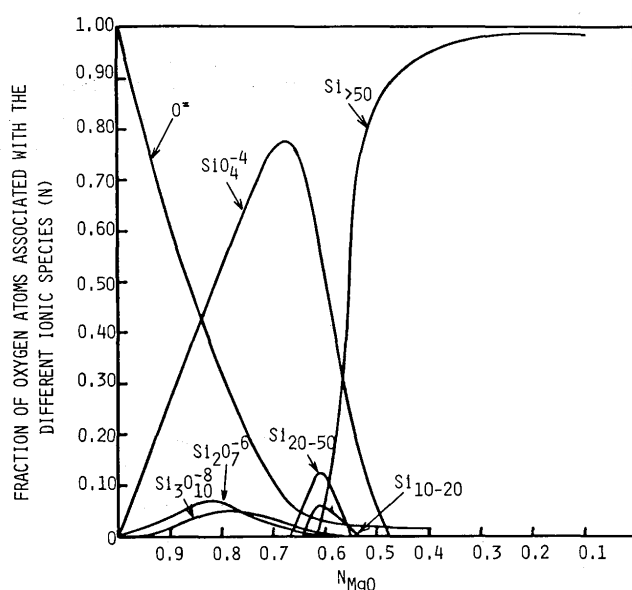
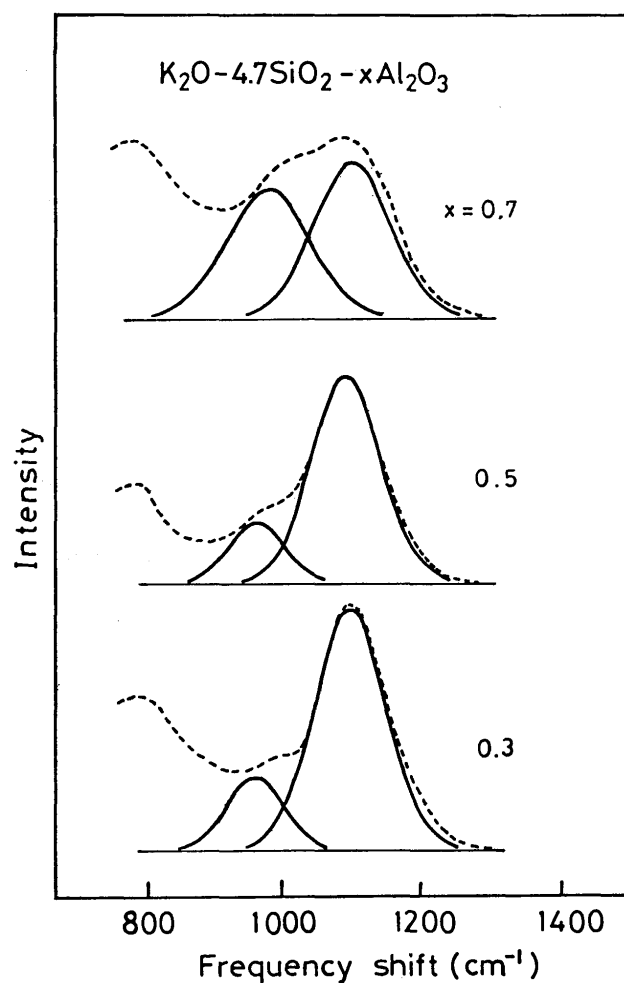Fig.10 Fraction of the oxygen associated with the different ionic species for the system MgO-SiO$_2$

Fig.11 Raman spectra of Na$_2$O-SiO$_2$-Al$_2$O$_3$ glasses separated into two Gaussian bands with the use of iterative least-square procedure
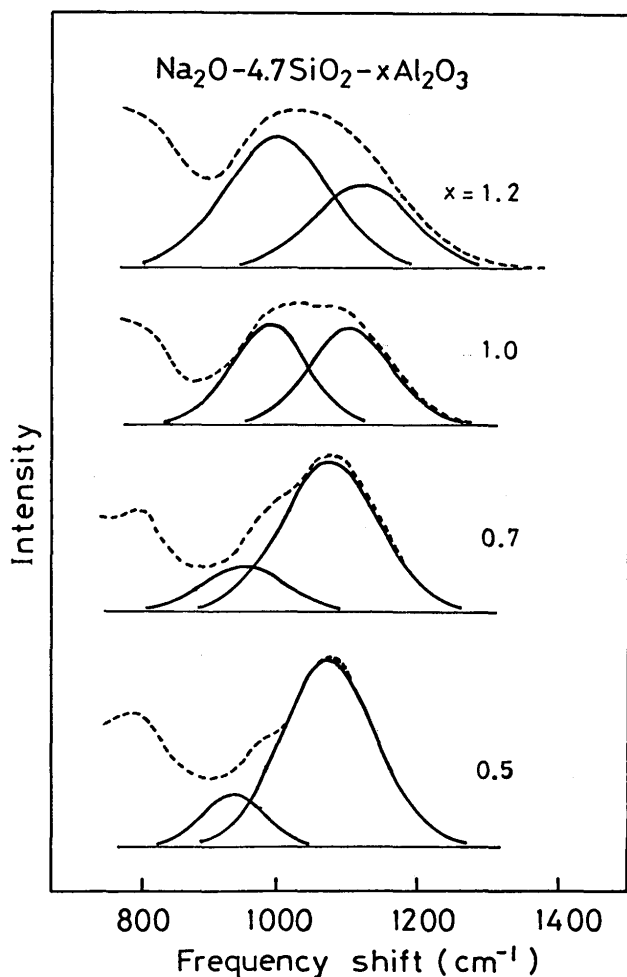

Fig.12 Raman spectra of K$_2$O-SiO$_2$-Al$_2$O$_3$ glasses separated into Gaussian bands with the use of iterative least-square procedure

(1)   the ionic refractivities of cations are constant,

(2)   high charged, small cations scarecely contribute to molar refractivity, and

(3)   the ionic refractivity of each of the three sorts of oxygens is constant for a particular glass system.

According to eq. (7), the change of the ionic refractivity of oxygen in glass per mole before and after that reaction can be expressed as $[2R_O{}^- - (R_O{}^\circ + R_O{}^{2-})]$, where $R_O{}^\circ$, $R_O{}^-$ and $R_O{}^{2-}$ are the ionic refractivities of bridged, nonbridged and free oxygen ions, respectively. If O° and O^{2-} are ideally mixed, the ionic refractivity of oxygen in a binary silicate glass equals ($2aR_O{}^\circ + bR_O{}^{2-}$). where a and b are the mole fractions of SiO$_2$ and a modifier oxide, respectively. When x mole O^{2-} reacts with x mole O°, producing 2x mole O^-, the following equation holds:

$$x [2R_O{}^- - (R_O{}^\circ + R_O{}^{2-})] = R_O{}^{ex} - (2aR_O{}^\circ + bR_O{}^{2-})$$

$$(14)$$

where $R_O{}^{ex}$ is the ionic refractivity of oxygen in glass determined experimentally. Rewriting the equation,

$$x = R_O{}^{ex} - (2aR_O{}^{e^\circ} + bR_O{}^{2-}) / [2R_O{}^- - (R_O{}^{e^\circ} + R_O{}^{2-}] \tag{15}$$

If **a** and **b** was selected so that **a** + **b** = 1, the ionic fractions of three sorts of oxygens can be calculated from the following relation:

$$N_O{}^\circ = 2a - x/2a + b, \quad N_O{}^- = 2x/2a + b,$$

$$N_O{}^{2-} = b - x/2a + b \tag{16}$$

'Ionic distributions of three sorts of oxygens in the system, Na_2O-, K_2O- and PbO - SiO_2 are shown in Figures (13) ~ (15), respectively. In these diagrams, the comparison with the result obtained by Kapoor and Frohberg[13] is done. Considerable discrepancies can be seen.

Fig.14 Ionic distributions of three sorts of oxygens in the system K_2O-SiO_2. The broken lines show the curves calculated using the equations after Kapoor and Frohberg with K=0.6
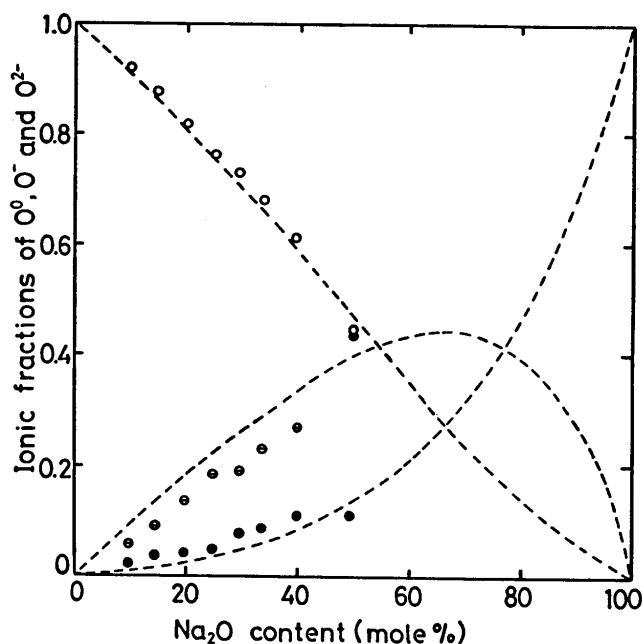

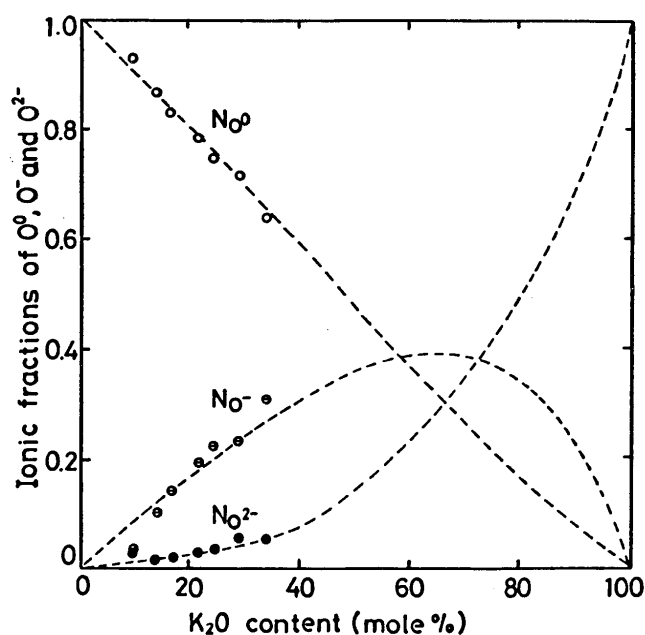
Fig.13 Ionic distributions of three sorts of oxygens in the system Na_2O-SiO_2. The broken lines show the curves calculated using the equations after Kapoor and Frohberg with K=0.4

2.2.2 Raman spectroscopy

Previously many investigators have applied IR (infrared absorption) method to solve the structure of silicate glasses, However it was difficult to obtain clear resolution because of the broad band. Recently as the intense Ar^+ ion laser was developed, it has become easily to solve the fine structure of spectra. The authors applied this mean on the systems, PbO [14] and CaO - SiO_2 [15].

Fig.15 Ionic distributions of three sorts of oxygens in the system PbO-SiO_2. The broken lines show the curves calculated using the equations after Kapoor and Flohberg with K=0.2

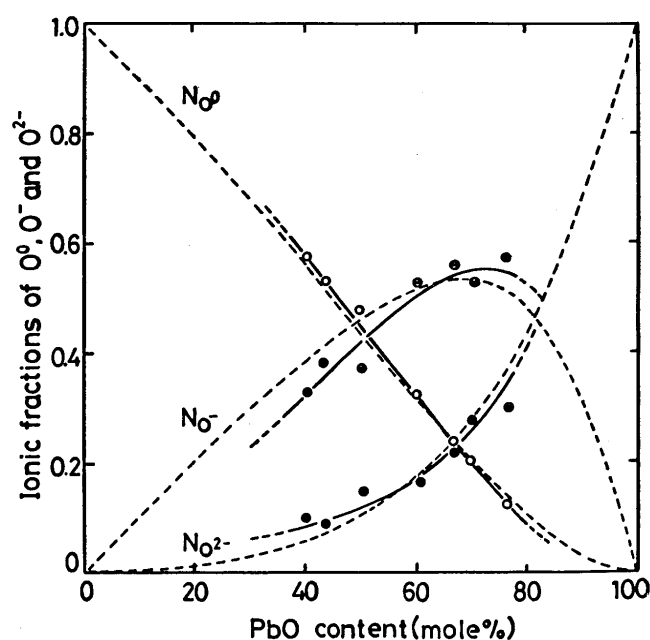By comparing with the infrared dielectric constant (E) obtained from the Kramers-Kronig analysis of reflectance of PbO-SiO_2 glasses, it is deduced that the band consists of five peaks near $8.9 \times 10^4, 9.2 \times 10^4, 9.6 \times 10^4, 10.3 \times$

10^4 and 11.5×10^4 m^{-1}. Furthermore, a comparison with the Raman and infrared absorption spectra of crystalline silicate suggests that these five peaks will arise from the SiO_4 tetrahedron with four, three, two, one non-bridged oxygens and with four bridged oxygens, respectively.

From this speculation, it becomes possible to calculate the fractions of three kinds of oxygens in a glass.

This calculation was performed with the following assumptions:

(1) The band due to Si - O stretching vibrational mode will be separated into same bands caused by the symmetry reduction of SiO_4 tetrahedron according to the addition of basic oxides.

(2) Each Raman spectrum from 800 to 1200 cm^{-1} was separated into four Gaussian bands at 880, 920, 975 and 1050 cm^{-1} in spite of the Lorentzian for harmonic oscillator.(CaO - SiO$_2$ system) As an example, ionic fraction of three sorts of oxygens are given with the comparison of the results by statistical thermodynamics in **Figure 16**.
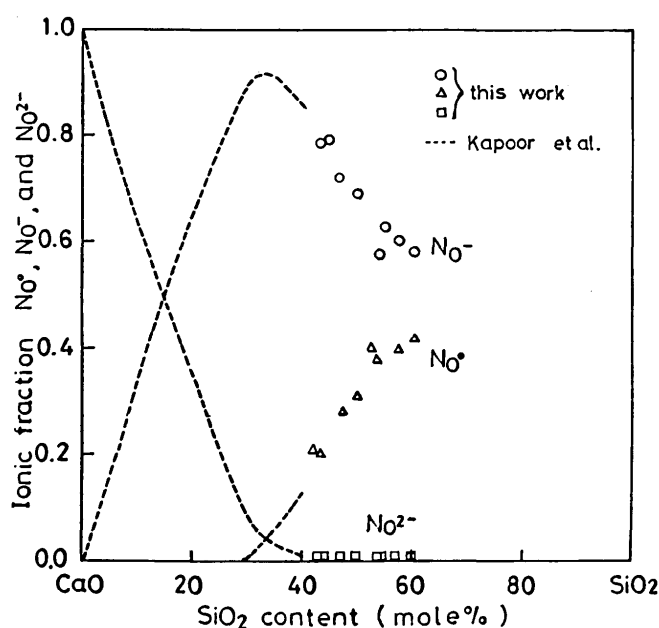

Fig.16 Ionic distributions of three sorts of oxygens in the system CaO-SiO$_2$. The broken lines show the curves calculated using data given with statistical thermo-dynamics by Kapoor, Mehrotra and Frohberg.

2.2.3 Spectroscopic means

Many investigators have applied X-ray spectrographic means to solve the structure of silica, silicates and oxides in the crystalline and vitreous state.[16][17] Although it became clear that the non-bridging oxygen gives influence on the electron density of all silicon atoms of the net-

work, the resolving power of that means is not sufficient to know fine structure about silicon and oxygen in glasses.

Brückner, Chun and Goretzki applied the means of photoelectron spectroscopy (ESCA: Electron Spectroscopy for Chemical Analysis) to measure the chemical shift of O 1s photoelectron lines of bridging and nonbridging oxygen atoms.[18][19] They paid attention on that the adsorbed gas molecule gives an important effect on the result and so that they attached breaking apparatus in analysing vessel and examined the freshly broken surface of glasses.

Kaneko and Suginohara applied this means on glasses of the system PbO - SiO$_2$.[20][21]

2.2.4 Trimetylsilyl derivative means

Lentz separated discrete · slicate anions in certain mineral and aqueous silicate solutions as their trimethylsilyl (TMS) derivatives by using gas-liquid chromatography.[22] Later Lentz[23], and Kolb and Hansen[24] applied this means on the study of portland cement and borate glass.

Götz et al modified this means by using trimethylsilyl choloride and applied to lead orthosilicate.[25]

Suginohara et al still modified this means and now continues the separation of various silicate anions.[26]

3. Summary

As previously written, a role of slag in welding, iron and steel-making is very important. Up to this time, no summarizing consideration on chemical reaction among gas, molten slag and metal has been given. From the viewpoints in various fields, the conculusion to proceed better chemical reaction can be drawn. In this review, the importance of the knowledge to determine ionic fractions of three sorts of oxygen in slag was emphasized. It is disappointed that to determine the fractions in the complex systems is difficult. It is also connected to provide the concept of basicity of slag.

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