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Author(s)	Iwamoto, Nobuya; Makino, Yukio; Funasaka, Hideyuki
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Study of Silicate Structure with Molar Refractivity[†]

Nobuya IWAMOTO*, Yukio MAKINO** and Hideyuki FUNASAKA***

Abstract

The state of oxygen was investigated from the ionic refractivity of oxygen in the several silicates. Ionic distributions of three species of oxygen were calculated from the ionic refractivity of oxygen on a few assumptions. In the system $PbO-SiO_2$, the calculated ionic distributions of three species of oxygen from ionic refractivity showed good agreement with that from the free energy of mixing. The results in the systems Na_2O-SiO_2 and K_2O-SiO_2 could not be compared with that from the free energy of mixing on account of no data. Further, it seems that ionic refractivity gives very effective information in order to investigate the state of oxygen around an amphoteric cation such as aluminium and titanium in silicate. However, it must be fully careful to induce the ionic distributions of three oxygen species in silicate from the use of ionic refractivity of oxygen.

1. Introduction

The roles of slag are very important in welding or metallurgical processes. In submerged arc and electroslag welding, the selection of flux gives decisive role on the mechanical properties of the welds. In the welding which flux is used, slag-metal reaction is one of the most important factor to decide the properties of weld metal. Then, the basicity of slag becomes the most important factor because the basicity of slag governs mainly slag-metal reaction. In other words, it is necessary to know the activity of free oxygen ion, $a_{O^{2-}}$ in slag. In general, $a_{O^{2-}}$ is determined from thermodynamical approach but such determination of $a_{O^{2-}}$ has been performed on the assumption such as Temkin model and so on. Further, the calculation of $a_{O^{2-}}$ has not been performed except the slag of the system $CaO-FeO-SiO_2$ ¹⁾ because of no thermodynamical data.

As above described, the basicity of slag is closely related to the state of ion, especially free oxygen ion, in slag. Therefore, to obtain $a_{O^{2-}}$ value is important to the clarification of slag structure. Structure of slag has been presumed from the various physical properties such as electronic conductivity²⁾, viscosity³⁾ and so on or from thermodynamical approaches^{1),4)}. Recently, new interpretations for slag structure have been obtained from spectroscopic measurements^{5),6)}. However, the state of oxygen ion in slag has scarcely been investigated except diffusion study of oxygen ion in slag.⁷⁾

In this study, the state of oxygen ion in several slags was investigated with ionic refractivity. Further, the distinction among free oxygen (O^{2-}), non-bridged oxygen

(O^-) and bridged oxygen (O^0) was performed on a few assumptions and the distributions of three species of oxygen were discussed in comparison with the results from thermodynamical consideration⁸⁾.

Following, the states of aluminium and titanium ion, which show amphoteric behaviour in slag, were considered from ionic refractivity of the nearest neighbouring oxygen around them. Three species of oxygen in slag can be distinguished with ionic refractivity of oxygen on the supposition that similar cation to silicon is not contained in slag. In other words, it must be assumed that all cations except silicon behave as modifier. However, when amphoteric oxide such as Al_2O_3 or TiO_2 is added to slag, the bridged oxygen such as $Si-O-Al$ and $Si-O-Ti$ and non-bridged oxygen such as $Al-O^-$ and $Ti-O^-$ can be produced because silicon site can be occupied by these amphoteric cations. Therefore, it is impossible to determine the ionic fractions of the three species of oxygen ion with ionic refractivity. However, it is expected that the state of the nearest neighbouring oxygen around cation can be distinguished with the molar refractivity of amphoteric oxide. Therefore, the states of aluminium and titanium ion in the systems $CaO-Al_2O_3-SiO_2$ and $K_2O-TiO_2-SiO_2$, respectively, were also investigated with molar refractivity.

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* Professor

** Research Associate

*** Graduate Student

2. Experimental Procedures

Each material used for the preparation of glassy slag was reagent grade SiO_2 , Al_2O_3 , Na_2CO_3 , K_2CO_3 and CaCO_3 . Most of specimens were melted at the temperature of 100°C higher than those melting points for 1 hr in platinum crucible, and then they were taken out into air and cooled. Several specimens with high viscosity were kept for 2 hr to 10 hr according to their viscosity. Density measurement was performed with Archimedean method. As immersion liquid, distilled water or toluen was used. Refractive index of specimen was measured with Abbe refractometer (Shimadzu Seisakusho Ltd., 3L type) using methylene iodide as the contact medium. Molar refractivity of slag was calculated from Lorentz-Lorenz formula $((n^2-1)/(n^2+2) \cdot M/d = R)$ and ionic refractivity of oxygen was calculated by subtracting ionic refractivities of cations from the molar refractivity of slag⁹. Ionic refractivities of oxygen in the systems $\text{Na}_2\text{O}-\text{SiO}_2$, $\text{K}_2\text{O}-\text{SiO}_2$ and $\text{PbO}-\text{SiO}_2$ were wholly or partly calculated from the data after Turnbull and Lawrence¹⁰, Rao¹¹ and Kordes¹², respectively.

3. Experimental Results and Discussion

1) Ionic refractivity of oxygen in binary silicate

In 1923, Wasastjerna¹³ calculated the ionic radius from molar refractivity. In 1939, Kordes^{14,15} proposed an empirical equation to give the relationship between the ionic radius and the ionic refractivity. From these results, he concluded that molar or ionic refractivity is related to the dimension of the molecule or ion. A small ionic radius and highly charged cation scarcely contribute to molar refractivity. In silicate such as slag, it can approximately be considered that the change of molar refractivity originates from the deformation of the large ionic radius anion such as oxygen. Therefore, it is expected that the variation of molar refractivity with the content of modifier oxide could give some informations about the states of the oxygen ion in slag.

As it can be assumed to be isotropic in glassy slag, Lorentz's localized field approximation¹⁶ can be applied. Hence, molar refractivities of amorphous slags were calculated from Lorentz-Lorenz formula. In the clarification of slag structure, it is very effective to know how the state of oxygen ion is influenced with the content of modifier oxide or with the species of modifier cation. Therefore, the purpose in this study was laid on the discussion with the measurement of molar refractivity in binary silicate such as $\text{M}_2\text{O}-\text{SiO}_2$ or $\text{MO}-\text{SiO}_2$ system, and the ionic refractivities of oxygen in the systems $\text{Na}_2\text{O}-\text{SiO}_2$, K_2O

SiO_2 and $\text{PbO}-\text{SiO}_2$ were compared. Figs. 1, 2 and 3 show the dependence of ionic refractivity of oxygen upon the content of modifier oxide in these binary systems. The calculated curve of ionic refractivity of oxygen in each slag regarded as ideal mixture is also shown.

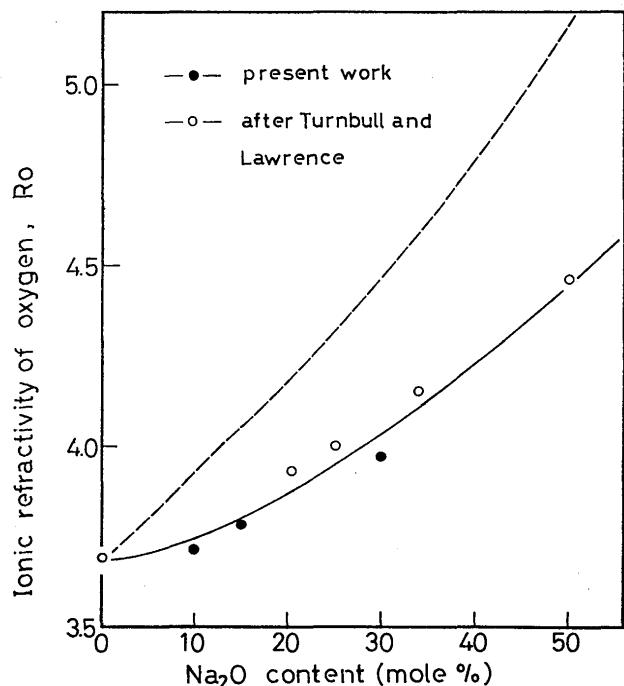


Fig. 1 Ionic refractivity of oxygen of the slags in the system $\text{Na}_2\text{O}-\text{SiO}_2$ (The broken line shows the ionic refractivity of oxygen in ideal mixing of O^0 and O^{2-})

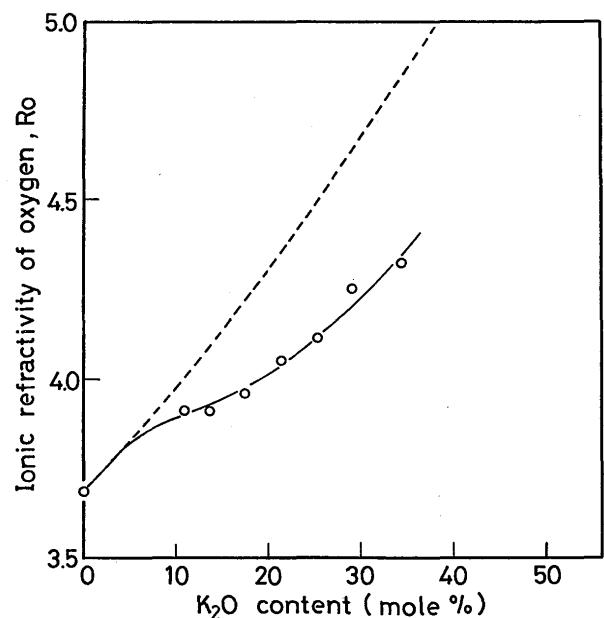


Fig. 2 Ionic refractivity of oxygen of the slags in the system $\text{K}_2\text{O}-\text{SiO}_2$ (The broken line shows the ionic refractivity of oxygen in ideal mixing of O^0 and O^{2-})

In Fig. 2, the curve of the ionic refractivity of oxygen is gradually close to the curve in ideal mixing with decreasing the content of K_2O . This phenomenon suggests that silica network does not change with the addition of K_2O when the content of K_2O is 10 mole per cent or less. Hence, the fact seems to correspond to the abrupt change of thermal expansion in binary alkaline-silicate¹⁷⁾ when alkaline metal oxide is over 10 mole per cent. However, some different result is obtained in the case of the system Na_2O-SiO_2 . Therefore, it is expected that the difference between sodiumsilicate and potassiumsilicate would be attributed to the difference of the field strength of cation.

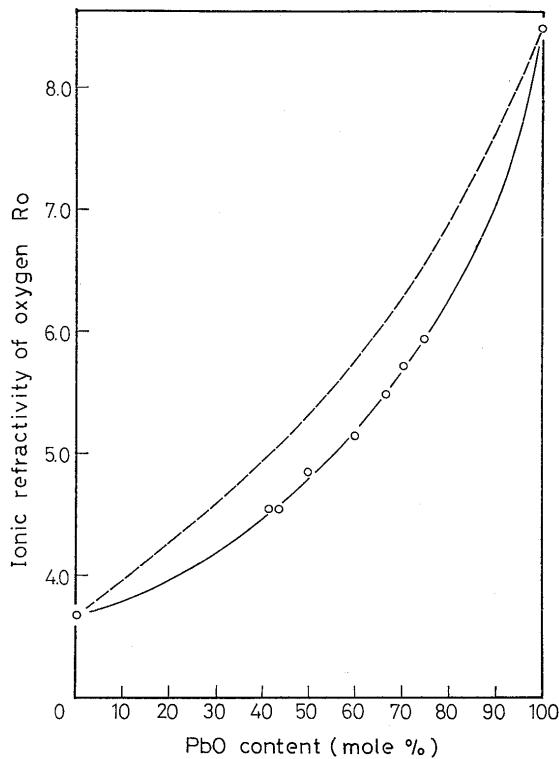


Fig. 3 Ionic refractivity of oxygen of the slags in the system $PbO-SiO_2$ (The broken line shows the ionic refractivity of oxygen in ideal mixing of O^0 and O^{2-})

Fig. 3 shows the ionic refractivity of oxygen in the system $PbO-SiO_2$ slag. Each plot was calculated from the data after Kordes¹²⁾. In this system, gradual approach to the curve in ideal mixing remains unclear on account of no investigation. It is an interesting phenomenon whether the gradual approach to ionic refractivity curve in ideal mixing is only appeared in the system K_2O-SiO_2 . Therefore, further investigation on other system is desired.

2) Ionic distributions of three species of oxygen in binary silicate

As described above, the content of free oxygen in slag is one of the most important factor to know the reactivity

of slag. From various results, it is presumed that the mole fraction of free oxygen ion, No^{2-} , would give the different value depending on the species of modifier cation. Toop and Samis¹¹⁾ semi-theoretically calculated the dependence of the three species of oxygen upon the content of modifier oxide from the charge and mass balance and the use of free energy value of mixing. Kapoor and Frohberg⁸⁾ indicated the shortcoming in the treatment by Toop and Samis and proposed the improved equations. Still several issues remain unclear in these propositions and it is necessary to verify these propositions experimentally. In this study, the dependence of ionic distributions of three species of oxygen upon the content of modifier oxide was determined with ionic refractivity of oxygen.

According to Fincham and Richardson¹⁸⁾, the reaction between free and bridged oxygens is expressed as follows:



Assuming that x free oxygens react to x bridged oxygens, $2x$ non-bridged oxygens are formed. When such a reaction occurs, the change of ionic refractivity of oxygen before and after the reaction equals to $[2Ro^- - (Ro^0 + Ro^{2-})] \cdot x$. This change must be equal to the difference between the experimental and calculated value when the ideal mixing is accepted. Hence,

$$x = \frac{Ro^{ex} - (2aRo^0 + bRo^{2-})}{2Ro^- - (Ro^{2-} + Ro^0)} \quad (2)$$

where Ro^{ex} : experimental value of ionic refractivity of oxygen

Ro^0 , Ro^- and Ro^{2-} : ionic refractivity of bridged, non-bridged and free oxygen

a and b : ionic fraction of silica and modifier oxide. As the number of non-bridged oxygen equals to $2x$, the number of non-bridged oxygen can be determined if only Ro^{ex} is measured. The number of free or bridged oxygen is determined by subtracting $2x$ from the initial number of free or bridged oxygen. Figs. 4 and 5 show the ionic distributions of three species of oxygen in the systems Na_2O-SiO_2 and K_2O-SiO_2 .

In these results, first of all, it becomes a subject of discussion whether the application of ionic refractivity value of oxygen obtained with crystalline state to glassy state is reasonable or not. Further, it comes also into question that the standard ionic refractivities of free or non-bridged oxygen are calculated from interionic distance or from molar refractivity of carnegite or orthorhombic $KAlSiO_4$. Standard ionic refractivities of three species of oxygen are shown in Table 1. In this study, it is assumed that all oxygens in crystalline orthosilicate are non-bridged oxygen. Olivine ($2MgO-SiO_2$) is a typical example which supports this assumption. However, it would be unreasonable to consider that only

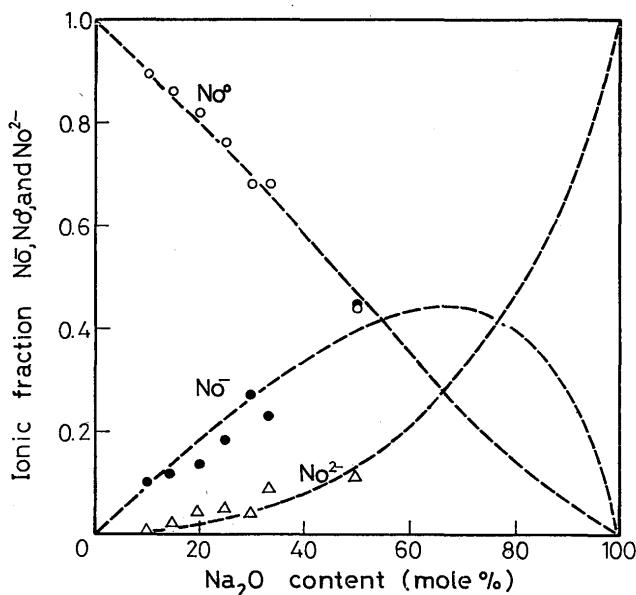


Fig. 4 Ionic distributions of three species of oxygen in the system $\text{Na}_2\text{O}-\text{SiO}_2$ (The broken line shows the calculated curve from the equations after Kapoor and Frohberg when $K=0.6$)

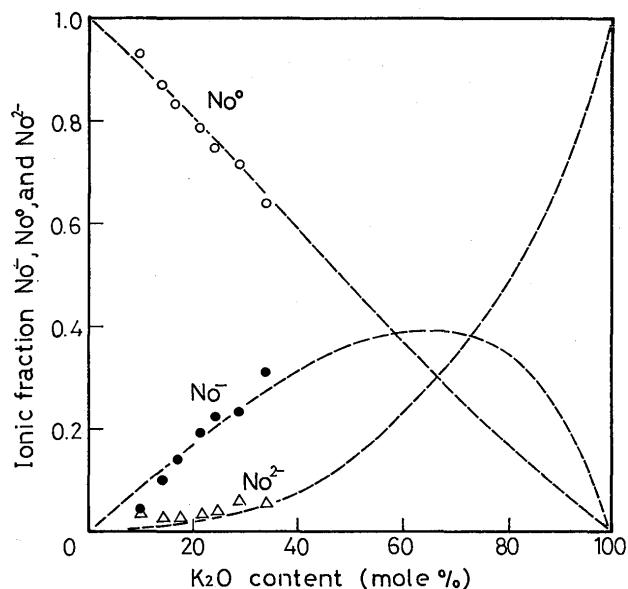


Fig. 5 Ionic distributions of three species of oxygen in the system $\text{K}_2\text{O}-\text{SiO}_2$ (The broken line shows the calculated curve from the equations after Kapoor and Frohberg when $K=0.4$)

Table 1 Standard ionic refractivities of three species of oxygen in three binary systems

	Ro^{2-}	Ro^-	Ro^0
$\text{Na}_2\text{O}-\text{SiO}_2$	8.124 from $r_o = 1.42\text{\AA}$	4.85 from carnegiite	3.683
$\text{K}_2\text{O}-\text{SiO}_2$	9.21 from $r_o = 1.46\text{\AA}$	5.46 from KAlSiO_4	3.683
$\text{PbO}-\text{SiO}_2$	8.51	4.68	3.683

non-bridged oxygen is formed in all crystalline orthosilicates.

According to Kapoor and Frohberg⁸⁾, the ionic fractions of three species of oxygen, No^0 , No^- and No^{2-} , are expressed as follows:

$$\text{No}^0 = \frac{2\text{NSiO}_2}{1 + \text{NSiO}_2} - \frac{\text{No}^-}{2} \quad (3)$$

$$\text{No}^- = \frac{1 - \sqrt{1 - \frac{8\text{NMO} \cdot \text{NSiO}_2(1-4K)}{(1 + \text{NSiO}_2)^2}}}{(1-4K)} \quad (4)$$

$$\text{No}^{2-} = \frac{\text{NMO}}{1 + \text{NSiO}_2} - \frac{\text{No}^-}{2} \quad (5)$$

where K is equilibrium constant.

K is determined from free energy value of mixing. Although Kapoor and Frohberg applied the equations (3), (4) and (5) to alkaline-earth silicate, in this study these equations were further extensively applied to alkaline silicate. Equilibrium constant in the systems $\text{Na}_2\text{O}-\text{SiO}_2$ and $\text{K}_2\text{O}-\text{SiO}_2$ became to equal to 0.6 and 0.4 according to their proposed equations. The concentration of free oxygen ion in the system $\text{K}_2\text{O}-\text{SiO}_2$ is a little higher than that in the system $\text{Na}_2\text{O}-\text{SiO}_2$ at the same modifier content. These equilibrium constants could not be compared with those from the free energy values of mixing because of insufficient thermodynamical data. Further investigation of free energy of mixing is desired in binary alkaline silicate.

The ionic distributions of three species of oxygen in the system $\text{PbO}-\text{SiO}_2$ were investigated as a typical example containing divalent modifier cation. Kapoor and Frohberg calculated the ionic distributions of three species of oxygen in this system by the use of equilibrium constant which was determined from the free energy value of mixing. As is shown in Fig. 6, the ionic distribution curves from ionic refractivity of oxygen showed good agreement with the curves obtained from equilibrium constant. With decreasing PbO content, the experimental curve of non-bridged oxygen gradually deviates from the curve which calculated from the equilibrium constant. Although various considerations can be given to clarify the inconsistency, it must be pointed out that the equilibrium constant is approximately expressed by the concentrations of three species of oxygen instead of the activities of them in the treatment by Kapoor and Frohberg. Further, it seems to be enough related to difficulty to form non-bridged oxygen in the region having much silica content.

Ionic refractivity of oxygen in the system $\text{CaO}-\text{SiO}_2$ was also investigated. In this paper, however, the detailed discussion could not be performed because the only incomprehensible result was obtained. It is suggested that the result in the system $\text{CaO}-\text{SiO}_2$ would propose some

doubts about the decision of the ionic distributions of three oxygen species from ionic refractivity.

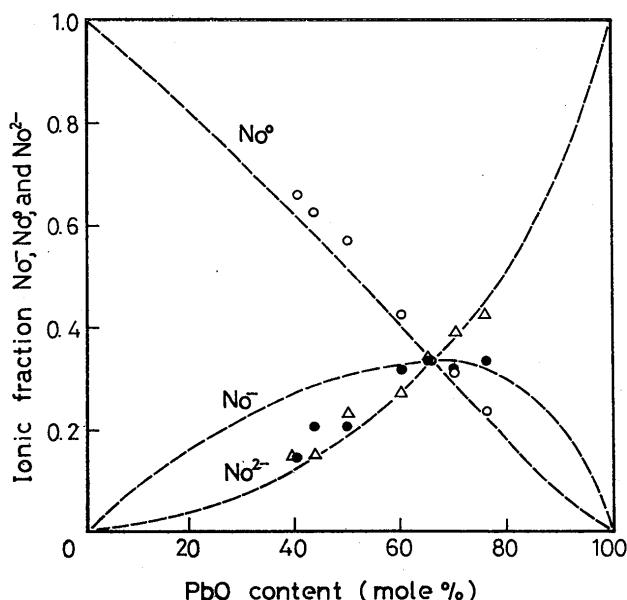


Fig. 6 Ionic distributions of three species of oxygen in the system PbO-SiO_2 (The broken line shows the calculated curve from the equations after Kapoor and Frohberg when $K = 1.0$).

3) Ionic refractivity of the nearest neighbouring oxygen around amphoteric cation

It is well-known that Al_2O_3 or TiO_2 in silicate has the characteristic behaviours. In aluminosilicate, for example, a strong ridge is found in the iso fract^{20),21)} and isoviscosity curve^{22),23)} and the dual role of titanium ion is also indicated in the silicate containing TiO_2 ¹¹⁾. As it is well established that aluminium ion can occupy every sites of four, five and six coordination in mineralogy, the characteristic behaviours have often been discussed in relation to the coordination of aluminium ion. Likewise, the dual role of titanium ion has also been considered to be attributed to the similar behaviour to aluminium.

The ionic refractivities of the nearest neighbouring oxygen around aluminium and titanium ion are shown in Fig. 7, 8 and 9. The result in Fig. 7 was calculated from the data after Rao¹¹⁾. Point A would be suspicious datum and, assuming that point A can be ignored, the ionic refractivity of the nearest neighbouring oxygen around titanium monotonously increases with increasing the content of TiO_2 except point B and C. Fig. 8 shows the result which was re-examined at a constant $\text{K}_2\text{O/SiO}_2$ ratio, and maximum point was appeared when $\text{K}_2\text{O/SiO}_2$ ratio nearly equals to unity. However, taking the inaccuracy in the refractive index measurement into account, the appearance of maximum point in Fig. 8

would be questionable. Hence, although some difference between Rao's and our result was recognized, it seems that the value of ionic refractivity of oxygen itself shows that of the nearest neighbouring oxygen around six-coordinated titanium ion.

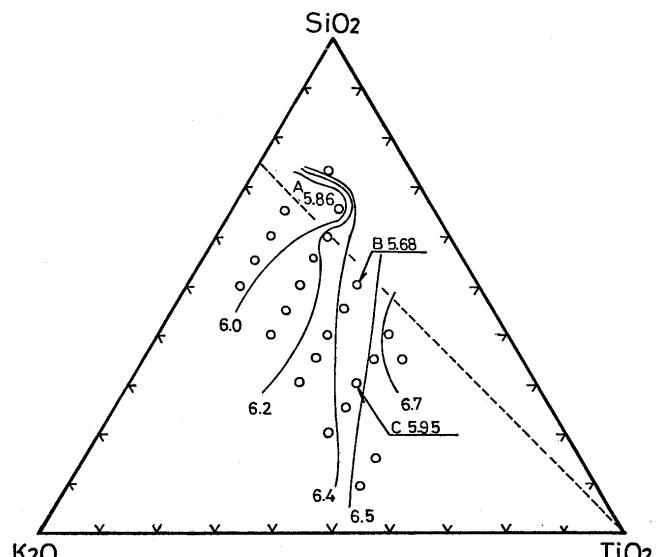


Fig. 7 Ionic refractivity of oxygen of the slags in the system $\text{K}_2\text{O-TiO}_2\text{-SiO}_2$ (after Rao¹¹).

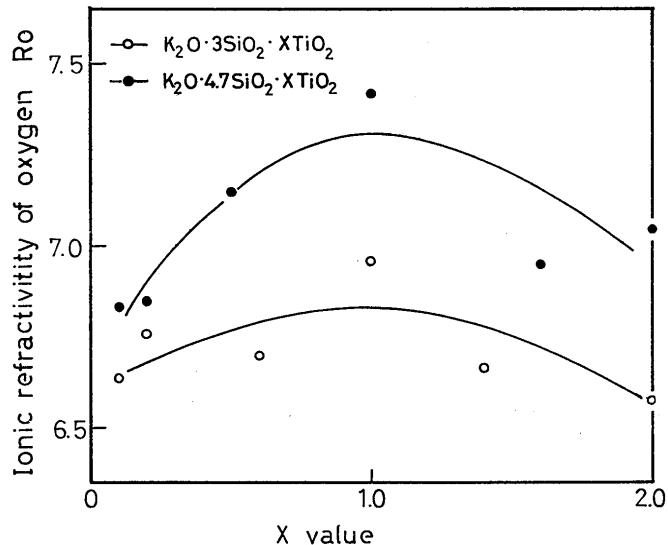


Fig. 8 Ionic refractivity of oxygen of the slags in the system $\text{K}_2\text{O-TiO}_2\text{-SiO}_2$

Ionic refractivity of the nearest neighbouring oxygen around aluminium ion showed a little higher value in anorthite field as shown in Fig. 9. In this case, the accuracy in the refractive index was about ten times better than that of the slag in the system $\text{K}_2\text{O-TiO}_2\text{-SiO}_2$ and the accuracy of ionic refractivity of oxygen in the system $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$ was within about 1 per cent. Therefore, the convex region in anorthite field is very significant and

it is suggested that the oxygen ion in the region is a little released when compared with that in other field. However, it is impossible to conclude that this convex region is originated to the coordination change of aluminium ion. The change in volume of oxygen ion could be also certified from the measurement of the ionic refractivity in the silicate slag containing amphoteric cation.

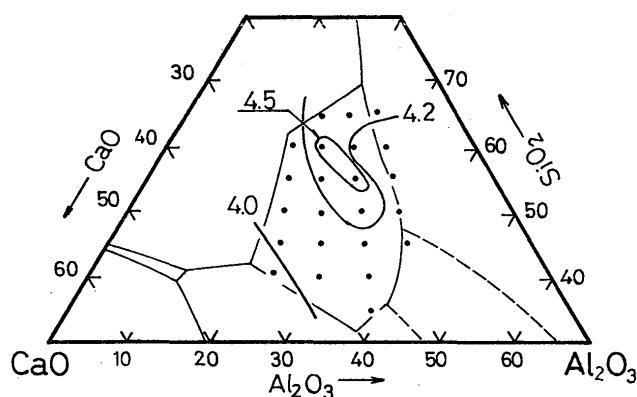


Fig. 9 Ionic refractivity of oxygen of the slags in the system $\text{CaO}-\text{Al}_2\text{O}_3-\text{SiO}_2$

4. Summary

The state of oxygen ion in silicate was investigated with ionic refractivity of oxygen and it was suggested that ionic refractivity can considerably clarify the state of oxygen ion in simple binary silicate such as $\text{Na}_2\text{O}-\text{SiO}_2$, $\text{K}_2\text{O}-\text{SiO}_2$ and $\text{PbO}-\text{SiO}_2$. Further, ionic distributions of three species of oxygen, O^0 , O^- and O^{2-} , were calculated from the ionic refractivity of oxygen on a few assumptions. Ionic distributions of three oxygen species in the system $\text{PbO}-\text{SiO}_2$ showed good agreement with the result from the free energy value of mixing which is proposed by Kapoor and Frohberg. The results in the systems $\text{Na}_2\text{O}-\text{SiO}_2$ and $\text{K}_2\text{O}-\text{SiO}_2$ could not be compared with those from the free energy value of mixing because of insufficient thermodynamical data. However, it must be fully careful to induce the ionic distributions of three species of oxygen from ionic refractivity measurement. Further, ionic refractivity was a fairly effective physical quantity in order to investigate the state of the nearest neighbouring oxygen around an amphoteric cation in silicate, but it seems that ionic refractivity can not easily detect the coordination change of amphoteric cation in silicate slag.

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