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Structure of Slag (Ⅳ)†
—Behaviour of Amphoteric Metal Ions in Slag—

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Abstract

Behaviour of amphoteric ions such as aluminium and titanium in slag have been considered with the results from various state analysis means. It has been emphasized that the behaviour of titanium ion in slag still remained unclear when compared with that of aluminium ion.

1. Introduction

As previously reported,1)−3) the concept of the basicity of slag still remains unclear despite the efforts of many investigators.

As logic, the problem can be resolved if we could know the activity of O^{2-} ion in slag. Recently Wagner says that the evaluation of emf measurement of cells involving slags is not recommended even if only an approximate measurement of the basicity of a slag is wanted.4)

In 1953, Tomlinson said that the solubility of CO_2 gas in slag is probably proportional to the activity of O^{2-} ion in slag.5)

Pearce measured the solubility of CO_2 gas in glasses of Na_2O-SiO_2 and Na_2O-B_2O_3 systems.6),7) Likewise, Holmquist studied the change of the solubility of SO_3 gas in glass of Na_2O-SiO_2 system.8) These sorts of studies seem worthy to obtain an effective information about slag structure.

In the welding division, it is especially important to know distribution coefficients of Mn/(MnO) and Si/(SiO_2) between metal and slag. Generally, it is now discussed from the viewpoint that there is interrelation between the distribution coefficients and the basicity of slag.9)−11)

As previously emphasized,1),2) the roll of the additives such as Al_2O_3, TiO_2 and CaF_2 on the basicity of slag is unknown, although these components are frequently used for flux in welding.

Accordingly, it is the purpose of this report to search new index explaining the interrelation.

In the glass technology, intermediate oxides including the ions of Be, Zn, Pb, Fe, Co, Ni, Ti, and Al have been paid our attention on the coordinated state in glasses.12)

Until now, we were continuously concerned with these problems. Therefore, I would like to give a certain direction to elucidate the behaviours of aluminium and titanium ions in slag.

2. Problem on aluminium ion in glass and slag

Schairer and Bowen originally measured the refractive index of glasses of Na_2O-SiO_2-Al_2O_3 system.13) From the isofracts obtained, it was determined that the bent occurs around the line connecting SiO_2 and $Na_2O/Al_2O_3 = 1$ as shown in Fig. 1. Galant found same tendency, that is, the break of refractive index occurred when the amounts of Al_2O_3 and Na_2O contained in the glass became equivalent.14) He simply said that aluminium can be four- or six- coordination according to the ratio of Al_2O_3 and R_2O in alkali aluminosilicate glasses.

Isard measured the electrical conductivities of soda aluminosilicate glasses.15) He found the occurrence of minima of activation energy for electrical conduction

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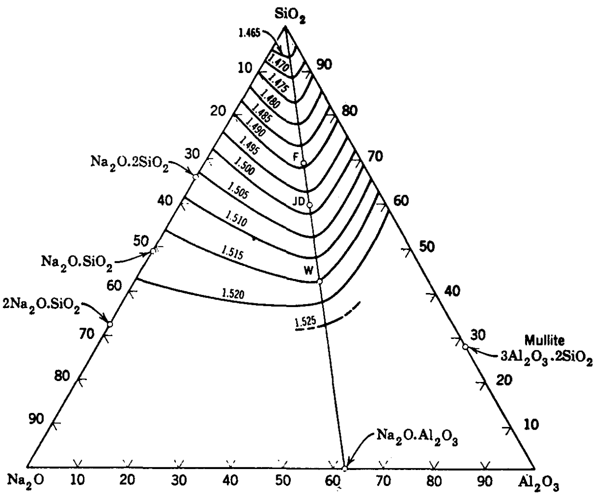

Fig. 1 Isofract lines of glasses in the Na_2O-SiO_2-Al_2O_3 system[13)]

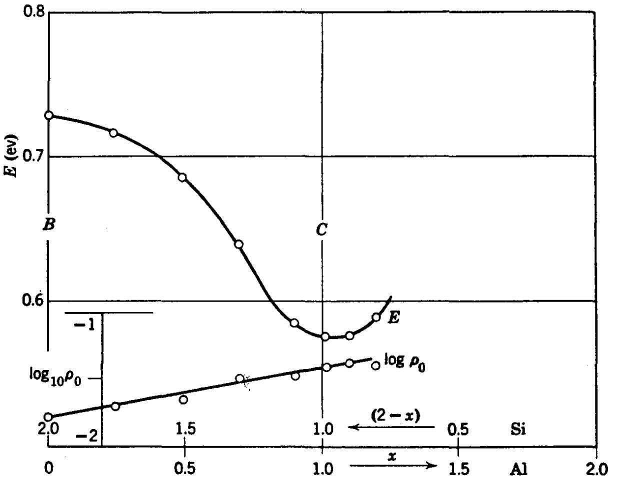

Fig. 2 Activation energies for electrical conduction in the Na_2O-Al_2O_3-SiO_2 system: Na-xAl-(2-x)Si. E=activation energy; ρ° = conatant term of electrical resistivity[15)]

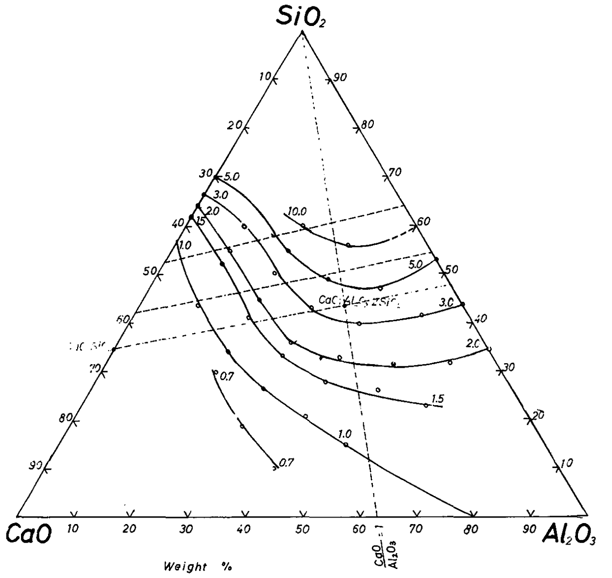

Fig. 3 Iso-viscosity lines of slags of CaO-SiO_2-Al_2O_3 system at 1900°C[16)]

when the Al/Na ratio equaled unity. The result is shown in Fig. 2.

Kozakevitch measured viscosity of CaO-Al_2O_3-SiO_2 system ranging widely of 1800 - 2100°C.[16)] As an example, iso-viscosity diagram at 1900°C is shown in Fig. 3. He found the similar tendency which produced the viscosity crest near the line $CaO/Al_2O_3 = 1$. The change was attributed to the difference between four- and six- coordination of aluminium ion in slag.

Kolesova studied the infrared absorption spectra of alkali aluminosilicate glasses and concluded that the absorption spectra resulted in the region near 760cm^{-1} of alkali aluminosilicate glasses commenced to develop two maxima with the increase of Al_2O_3 content of glass.[17)]

Saksena performed the infrared absorption studies of some silicate minerals and he paid his attention on the problem of Al-O bonds.[18)] As his conclusion, it was presented that it was impossible to distinguish four- or six-coordination of aluminium ions from the infrared absorption study.

Tarte classified the main absorption of XO_4 and XO_6 as follows:[19)]

Table 1 Characteristic frequency of some coordinated groups[19)]

Cation X	Absorption range (cm^{-1})			
	XO_4 tetrahedra		XO_6 octahedra	
	Condensed	Isolated	Condensed	Isolated
Ti^{IV}		800 - 690	650 - 500	<500 (?)
Al	900 - 700	800 - 650	650 - 500	530 - 400

In the complex aluminosilicate, the force constants of the Al-O bonds of AlO_4 tetrahedra are rather lower than those of Si-O bonds, but generally the vibrations give a composite absorption band including both Al-O-Si and Si-O-Si stretching vibrations in the 900–1100cm^{-1} region, which shifts to lower frequencies with increasing aluminium for silicon substitution.

Day and Rindone said that the four-fold coordination state of the aluminium ions which do not precipitate in the tetrahedra network could occasionally be surrounded by five, six, or seven oxygen ions and have an average coordination number of six.[20)] Accordingly, they said that the fact, which the infrared absorption spectra of glasses having an Al/Na ratio greater than unity did not contain an absorption band, could be assigned specifically to AlO_6 groups.

Tarte summarized that the picture is incomplete as six-fold coordination by infrared absorption spectroscopy for several reasons:

1) The characteristic frequency range is generally not so well delimited as in the case of four-fold coordi-

nation.

2) These vibrations are generally located in the low frequency region, the experimental study of which is difficult.

Besides the difficulties inherent to the study of the groups with high coordination numbers, the application of infrared spectroscopy to structural studies of slag suffers from more general drawbacks such as:

1) Lack of sensitivity, especially due to the broadness of the bands.
2) Difficulties in the correct assignment of the bands: in some cases, it is quite impossible to choose between several interpretations.[19)]

For these reasons, it became advisable to obtain low frequency Raman bands using more powerful and monochromatic excitation laser sources.

Our results of IR and Raman spectra are compared in Figs. 4 and 5.[21)–23)] From these spectra, it will be understood that the views above described are correct.

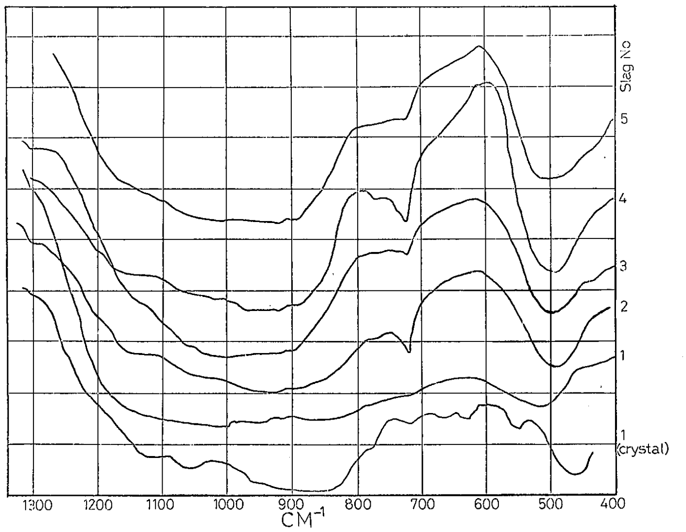

Fig. 4 Infrared spectra of the slags in the case of $CaO/SiO_2 = 0.71$[21)]

Mole%

Slag No.	TiO_2	SiO_2	CaO
1	15.5	49.3	35.2
2	11.4	51.7	36.9
3	7.5	54.0	38.5
4	3.7	56.2	40.1
5	0	58.3	41.7

The Lorenz-Lorentz equation is used to calculate the molar refractivity of each specimens from the density and refractive index. As the additive rule is assumed to hold, the partial molar refraction of the components added can be deduced. Molecular refraction for visible light is a measure of the deformation or distortion of the electron shells in the structure units. Accordingly, it becomes possible to estimate the change of metallic cations coordinating in slag from the information. This subject was treated by Fajan in detail.[24)] The application to glasses were carried out by three groups until now.

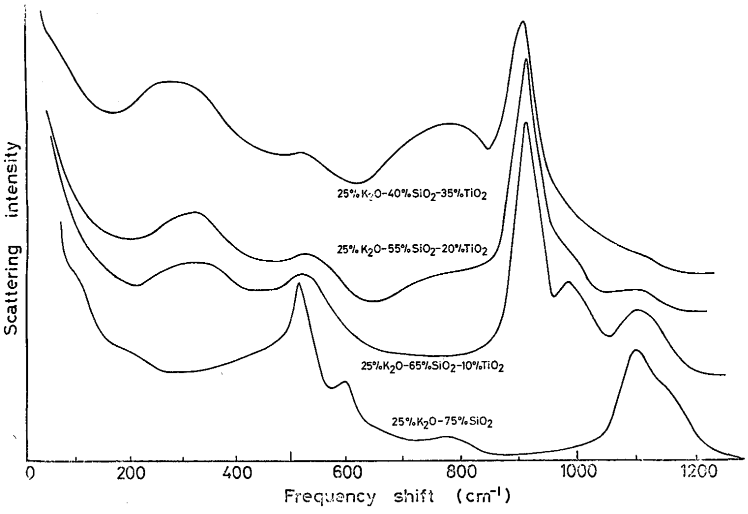

Fig. 5 Raman spectra of potassium titanosilicate glasses (K_2O, 25wt% series)[23)]

Safford and Silverman,[25)] and Day and Rindone[20)] treated the coordination problem of aluminium ion in glasses. However they failed to certify the existence of aluminium ions as six-fold state because of the experimental inaccuracies of the values of density and refractive index.

Turnbull and Lawrence[12)] studied the effect of TiO_2 addition to the systems, $Na_2O{\cdot}2SiO_2{\cdot}XTiO_2$ and $Na_2O{\cdot}4SiO_2{\cdot}XTiO_2$ on the partial molar refractivity of TiO_2. As an example, the effect of TiO_2 content on total refraction of a $Na_2O{\cdot}2SiO_2{\cdot}XTiO_2$ glass is shown in Fig. 6. From the result, it will be seen that there never occurs the abrupt change when the ratio TiO_2/Na_2O becomes more than unity. It was concluded that

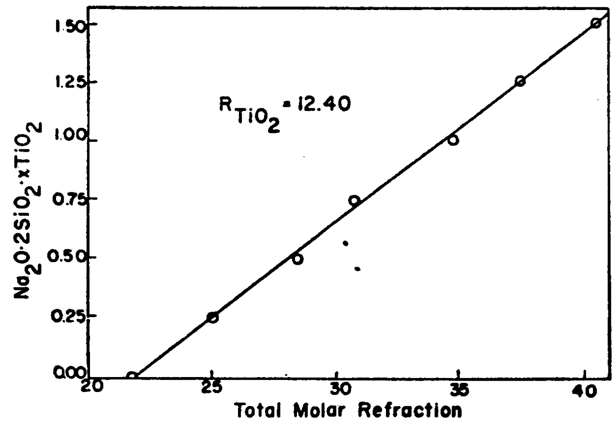

Fig. 6 Effect of TiO_2 content on total refraction of a $Na_2O{\cdot}2SiO_2{\cdot}xTiO_2$ glass. Slope of curve indicates R_{TiO_2}[12)]

TiO_2 by itself is not a glassformer but in the presence of silicon may enter into the network structure.

It has been well known that the information on the emission X-ray peak shift is effective to determine a change in the valence of an element.

Day summarized peak displacements of 0.04 to 0.06°(2θ) and 0.08 to 0.12°(2θ) for compounds having aluminium ions in fourfold and six-fold coordination respectively.$^{26)}$ His result is shown in Fig. 7. Brindlay and McKinstry noticed that X-ray peak displacement is suffered a considerable influence due to the kind of anion surrounding an aluminium ion.$^{27)}$ Experimental results obtained by us are given in Table 2.$^{28)}$ From this, it will be understood that aluminium ions in the Na_2O-SiO_2-Al_2O_3 and CaO-SiO_2-Al_2O_3 systems take four- or six-fold coordination depending on MO/Al_2O_3 ratio of slag composition from the comparison with the result in Fig. 7.

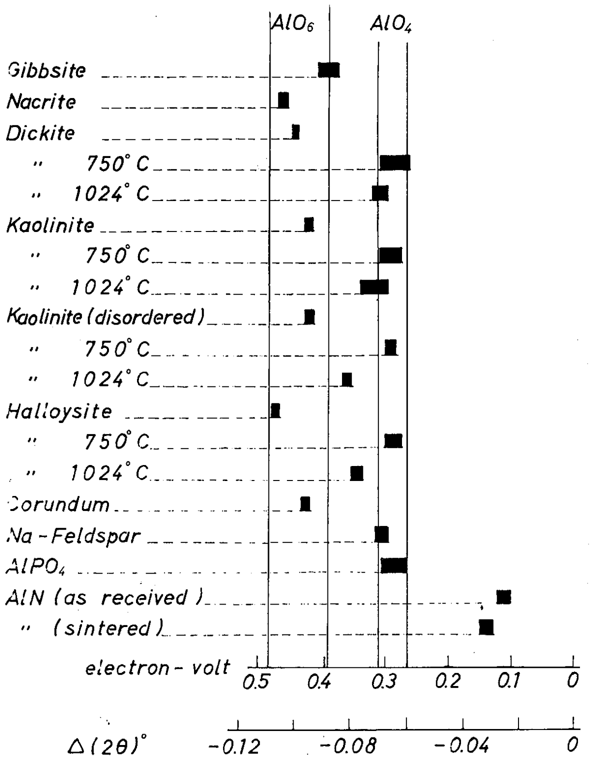

Fig. 7 X-ray peak shifts of Al ions in various minerals$^{26)}$

Table 2 X-ray peak shift of AlKα ($\Delta^{\circ}2\theta$)

Specimens		$\Delta^{\circ}2\theta$
Na_2O-Al_2O_3-SiO_2	10- 9-81	0.052
	10-27-63	0.061
	50- 5-45	0.060
	50-15-35	0.064
CaO-Al_2O_3-SiO_2	16-34-50	0.066
	30-20-50	0.055

Lacy proposed the term, total oxygen density, of glasses.$^{29)}$ His attention was especially focused upon oxygen packing, its dependence upon the nature of the metallic cation and upon the atomic proportion of silicon. Given the density and composition of a silicate the absolute number of oxygen ions in a unit volume (c.c.) of the solid can be readily calculated. For ease of discussion, the absolute number divided by a factor of 10^{20} is called the "oxygen density" of the solid. In certain computations it may be necessary to consider the volume of the cations in a structure relative to that of oxygens. Cation density is converted to "equivalent oxygen density" and it is added to "oxygen density". That is called as "total oxygen density". In Fig. 8, the iso-total oxygen density curves are shown on the slags of CaO-SiO_2-Al_2O_3 system.$^{28)}$ It will be anticipated that similar tendency of the bend taking place arround the line connecting SiO_2 apex and $CaO/Al_2O_3 = 1$.

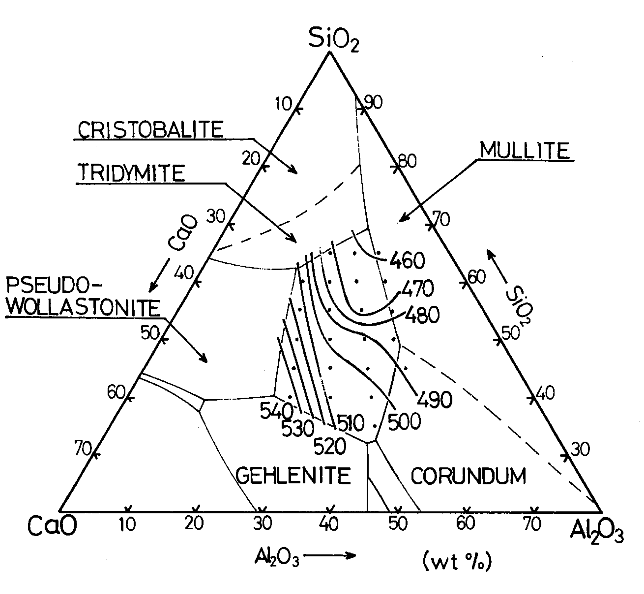

Fig. 8 Total oxygen density diagram of the CaO-Al2O3-SiO2 system$^{28)}$

3. Problem on titanium ion in glass and slag

In the welding, TiO_2 is widely used as additive for the welding flux because it gives flux to have proper viscosity characteristic.

On the other hand, it has been said that in the blast furnace operation with the slag containing titanium ion troublesome problem occurred because of highly viscous slag formation. These contradictory results are still unresolved.$^{30)}$

Hellbrügge and Endel showed the contrary additive effect of TiO_2 and SiO_2 on the viscosity of $Na_2O \cdot 2SiO_2$ glass.$^{31)}$ The former decreases the viscosity coefficient, but the latter increases. From these results, it is difficult to recognize the similar action in glass or slag between TiO_2 and SiO_2.

Frohberg and Schenck have investigated in detail on the viscosity coefficient of CaO-SiO_2-TiO_2 and Al_2O_3-SiO_2-TiO_2 system.[32] The followings are their conclusions. It was noticed that SiO_2 content has great influence on the viscosity in Al_2O_3-SiO_2-TiO_2 system, but viscosity does not change noticable in the case of low TiO_2 content. On the other hand, the isoviscosity lines are parallel to the variation of Al_2O_3 in the case of CaO-Al_2O_3-TiO_2 system. CaO content gives additional effect to the influence of TiO_2. They have summarized that TiO_2 generally decreases viscosity of the slag which contained CaO, SiO_2, and Al_2O_3.

Secondary, the results of electrical conductivity measurements will be briefly described. With increasing TiO_2 content in Na_2O-SiO_2-TiO_2 system, electrical conductivity decreases, but the value increases in CaO-SiO_2-TiO_2 system, It seems as if Ti^{4+} ion makes Ca^{2+} ion free from the silicate network. However, in FeO-SiO_2 system, electrical conductivity decreases with increasing of SiO_2, but increases with the addition of TiO_2.[33],[34]

Turnbull and Lawrence concluded that the role of TiO_2 in silica glass resembled to that of crystals in which the coordination number is six from the measurement of density and refractive index.[12]

On the contrary, Rao presented the results that the Ti^{4+} ion is a network-former in its own right and is capable of taking part in the network in tetrahedral and octahedral coordination, depending on conditions from the various measurements such as oxygen packing, expansivity, viscosity and tensile strength.[35]

Whereas, Rao said that the coordination of titanium would be changed from six to five in the transformation of $BaTiO_3$ and $PbTiO_3$.

From the viewpoint of glass-ceramics, many investigators took note of TiO_2 addition to various glasses. Mackenzie and Brown[36] compared octahedral site preference energy for titanium ion in aluminosilicate with the published values by McClure[37] and Dunitz and Orgel.[38] From this they concluded that octahedral site preference energy of titanium ion is lower than Al^{3+}, therefore, it is in predominantly tetrahedral site. Kondratev mentioned that titanium begins to enter the aluminosilicate structure in the form of $[TiO_4]$ units, when the amount of TiO_2 introduced into the glass exceeds the amount of aluminium oxide in octahedral coordination.[39] Further, during repeated heating titanium tends to supplement its oxygen deficiency by some displacement of the atoms around the $[TiO_4]$ units, which are converted into deformed $[TiO_6]$ units. According to Galant, oxygen ions from alkali or alkaline earth oxides available in TiO_2 are sufficient for formation of $[TiO_4]$ polyhedrons, and therefore, it can be assumed that titanium retains the coordination number of six in the glass.[40]

Our result shown in Fig. 5 explained that the band at 280 and 770cm^{-1} became more obvious which were probably attributed to the intrinsic character of rutile TiO_2 with increasing TiO_2 content.[22],[23]

Probably TiO_4 and TiO_6 units will be formed in slag of K_2O-SiO_2-TiO_2 system. X-ray peak shift study, refractive index and X-ray absorption measurements are described in our papers.[21],[22]

4. Summary

The influence of the coordination state of cations in slag on the physical and chemical properties of slag is important matter.

Furthermore, detailed studies such as gas solubility, surface property and so on are wanted.

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