Structure of Slag (V)[†]

— Gas Solubility of Slag —

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Abstract

The structural change in slag which contains amphoteric oxide such as Al_2O_3 and TiO_2 was considered from the information concerning gas solubility of water and nitrogen. It was emphasized that the contribution of Al_2O_3 and TiO_2 to the water solubility of the CaO-SiO_2 system was different. It was shown that the solution behaviour of water with Al_2O_3 addition differs depending on CaO/SiO_2 ratio.

1. Introduction

When we consider the chemical reactions in the iron-, steel-making and welding processes, the following reactions such as gas-molten metal, gas-molten slag and molten slag-molten metal should be considered not as being independent but as a respectively combined form.

In the field of welding, our attention is aimed into the penetration of gases to the welded products: 1) hydrogen which causes to hydrogen embrittlement, 2) oxygen and nitrogen which give harmful effect on the impact value of the products. Furthermore, it is serious problem that the reaction temperature is higher and especially the solidifying velocity is faster when compared with iron- and steel-making.

Based upon many years' experience, almost same composition of flux in welding with the slags in iron- and steel-making has been used although there exist a few exceptions in submerged arc and electro-slag welding.

As afourmentioned, the same deoxidizing effect in welding as iron- and steel-making shall not be expected. because the solidifying velocity of weld metal is too faster to permit the rising separation of the deoxidation products.

Besides, it is required to fulfil another conditions such as weldability to obtain good bead shape. Accordingly, it is natural that the flux composition has been experimentally chosen since old time.

Today, we should pay our attention to choose the flux composition to minimanize the gas content in weld metal theoretically because the demand of the steel having high quality is being desired for the use under severe circumstance.

The author have summarized the structure of slag in several papers[1]~[4], and think that the solution behaviour of gases in slag gives insight to solve the structure o slag from another viewpoint.

In this review, the author put emphasis on the relationship between amphoteric oxide and the solubility of gases in slag.

2. Solution of water vapor in oxide melt

Since olden time, many papers concerning the solution of hydrogen in glasses have been published[5]~[7]. On the other hand, there was few paper treated the solution of water vapor in synthetic slag[8].

Franz and Scholtz[9] corresponded their result and the results by several investigators[5]~[8]. As shown in Fig. 1[9], their result did not show the occurrence of minimum solubility. They induced the cause of minimum appearence to the vaporization of Na_2O component in the experiment. At first, Uys and King discussed the relationship between the basicity of slag and the solubility of water vapor[10],[11].
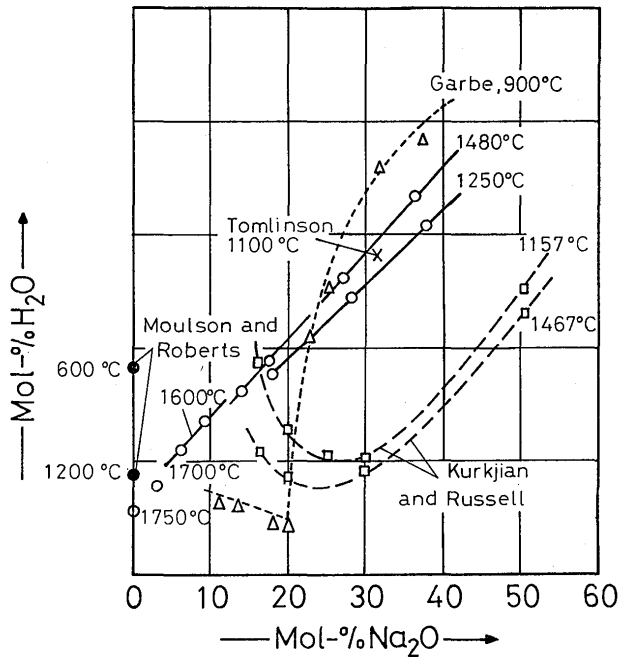
Fig. 1   The solubility of water vapor in glass of the Na$_2$O-SiO$_2$ system[9].

Fig. 2   Relationship between the time for water vapor vapor and the content of basic component[10].

Their results are shown in Fig. 2[10]. It will be seen that silicates containing Li$^+$ and Ca^{2+} cations increase the water solubility with the increase of basicity than orthosilicate, but for silicates containing Zn^{2+}, Fe^{2+} and Co^{2+} cations decrease the water solubility as the basicity increased. When the attraction between the metal cations and oxygen ions and the water solubility at metasilicate
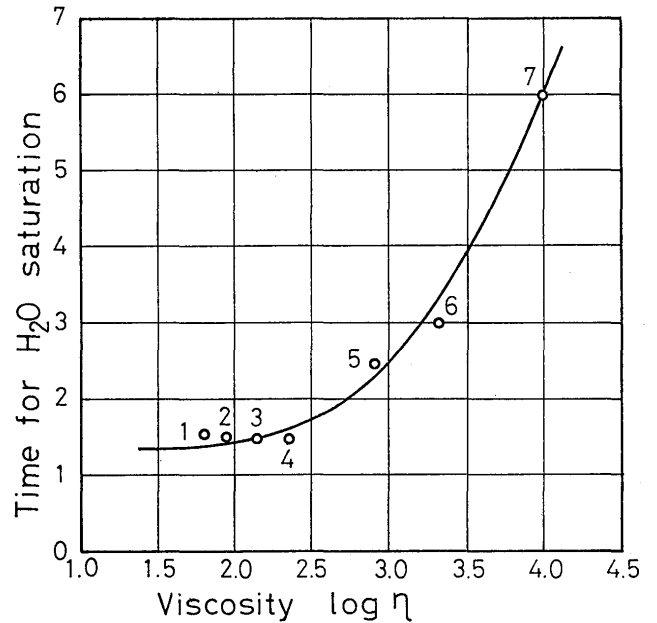

Fig. 3   Relationship between the time for water vapor saturation and the viscosity of glass[9].

No.	Composition	Temp. (°C)
1	Na$_2$O:SiO$_2$ = 20.80	1450
2	Na$_2$O:CaO:SiO$_2$ = 16:10:74	1450
3	Li$_2$O:SiO$_2$ = 20:80	1450
4	K$_2$O:SiO$_2$ = 20:80	1450
5	K$_2$O:SiO$_2$ = 10.7:89.3	1480
6	K$_2$O:SiO$_2$ = 7.5:92.5	1480
7	K$_2$O:SiO$_2$ = 5.1:94.9	1480

composition (MO·SiO$_2$) was compared, water solubility is larger for those melts containing cations with a weak attraction for oxygen ions. In this case, ion-oxygen attraction parameter I[12] is defined as follows:

$$I = 2Z^+/a^2 \qquad\qquad (1)$$

where Z$^+$ is the cation valency and a the internuclear distance, according to Pauling[13], between the cation and oxygen in the appropriate coordination.

Scholtz endeavored to determine water vapor solubility from infrared absorption band[14]. He recogneized three bands, 2350, 2850 and 3500 cm^{-1}, which originated from OH band, and obtained the extinction coefficient ϵ.

$$\log 1/T = \epsilon \, cd \, (T = I\lambda/Io\lambda) \qquad (2)$$

where Ioλ is initial wave intensity, Iλ wave intensity after transmission, c the hydrogen content and d the specimen width respectively.

As is evident from Fig. 3[9], the lower viscosity of glass is, the longer equilibrating time for water saturation is necessary. In general, we can make the following state-
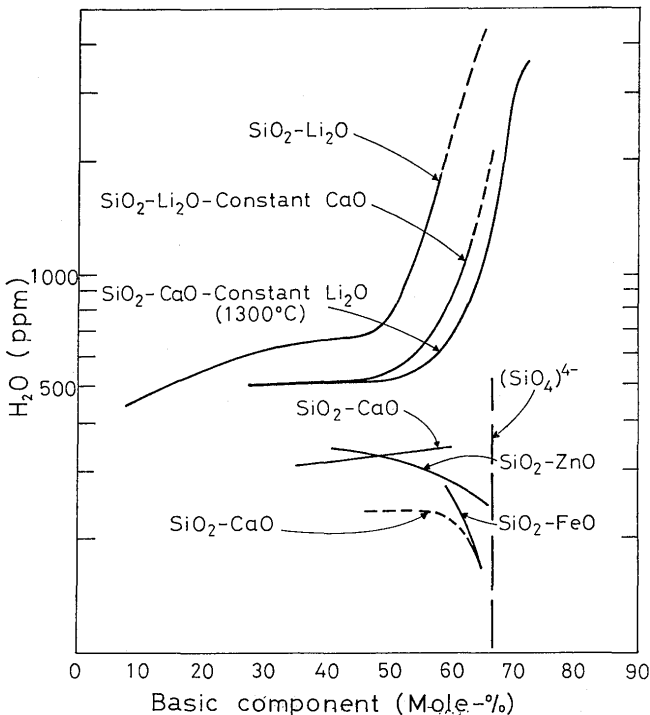
ment that molten oxide having lower viscosity easily forms newer surface to solve water.

Meanwhile, the strongest correlation was observed between the solubility of water in binary silicate glass and the sort of alkali metal oxide added. That is, the greater ionic radius of alkali metal is, the steeper the gradient of the solubility of water becomes. To be greater ionic radius of alkali metal means the decrease of field strength between cation and oxygen (I). (Fig. 4)

In the case of glass in ternary silicate ($R_2O \cdot RO \cdot SiO_2$), it was admitted that the solubility of water increased with the increase of ionic radii of alkaline earth metal as follows:

$$Mg < Ca < Sr < Ba$$
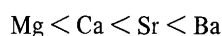
when the content of Na_2O or K_2O was kept to be constant.

Fig. 5   The solubility of water vapor in the glass of the system $Na_2O\text{-}CaO\text{-}SiO_2$ system at $1400°C$[9]. ($Mol\text{-}\%H_2O$)
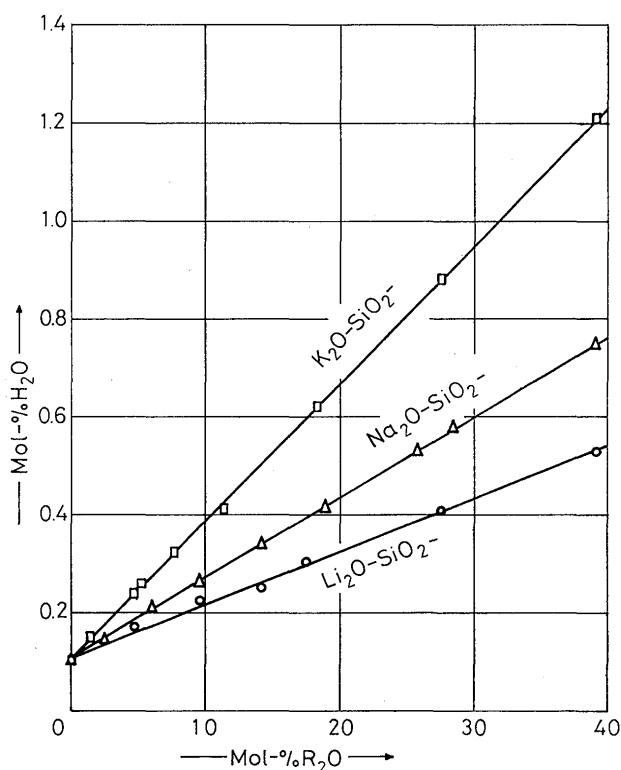
Fig. 4   The solubility of the glass of the $R_2O\text{-}SiO_2$ (R=Li, Na, K) system at $1700°C$[9]. ($P_{H_2O}= 760$ Torr)

In Fig. 5[9], the solubility of water in the $Na_2O\text{-}CaO\text{-}SiO_2$ system at $1400°C$ is shown. It was confirmed that the solubility of water at constant SiO_2 decreased when Na_2O was substituted with CaO. Besides, it was proved that the solubility of water at constant alkali metal oxide did not show any change when SiO_2 was exchanged with CaO.

With the use of temperature dependence on the solubility of water, the following heat of solution was obtained:

binary system, 3 ~ 6 Kcal/Mol
ternary system, 1 ~ 3 Kcal/Mol.

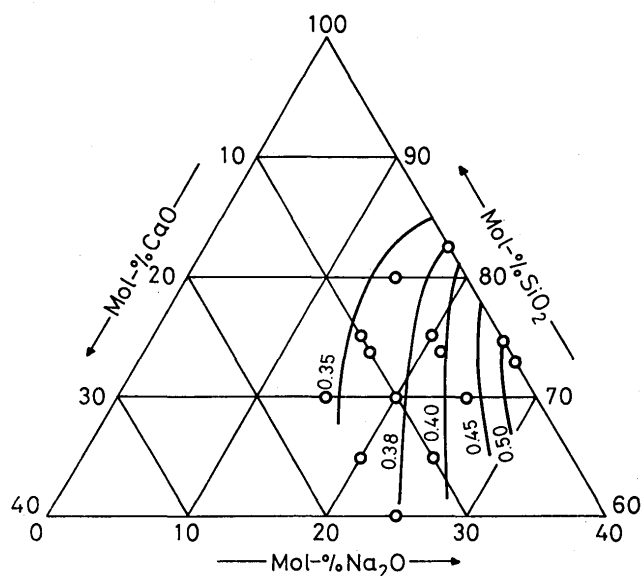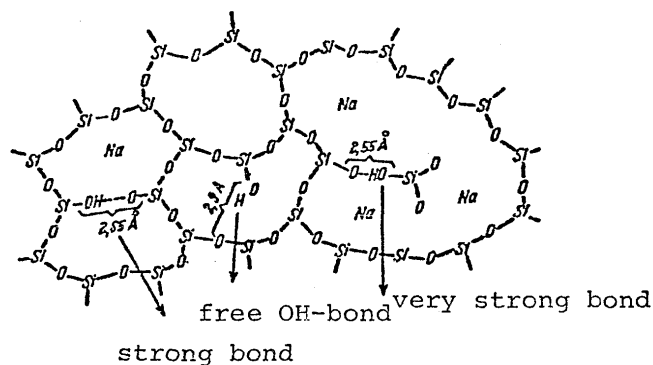free OH-bond   very strong bond

strong bond

Fig. 6   Schematic representation of various sorts of OH-group in the $Na_2O\text{-}SiO_2$ glass.[15]

From the result, it was anticipated that the solubility of water increased with the temperature rise.

From the fact that the solubility of water is proportional to the square root of the partial pressure of water vapor, the following solution mechanism is offered.

$$H_2O \text{ (gas)} + O^{2-}\text{(melt)} = 2OH^- \text{ (melt)} \qquad (3)$$

According to the various investigators, Scholze and his cooperators[9], [14]~[19], Novochatskij, Esin and Chuchmarev[20], and Imai, Ooi and Emi[21], it is thought that the following three forms occur in glass and slag.

(1) free-OH group
(2) OH group having strong hydrogen bond (O—O distance=2.6~2.7Å)
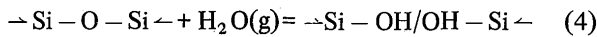(3) OH group having very strong hydrogen bond (O—O distance = 2.5Å)

The situations are shown in Fig. 6[15].

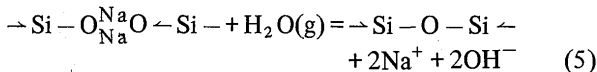Kurkjian and Russel[6] certified the appearence of

minima in the relation, the solubility of water vs. alkali metal oxide content. From the solution-behaviour, it was thought that there exist two different solution-mechanisms in glass.

Russel[22] and Tomlinson[5] presented the following solution mechanism.
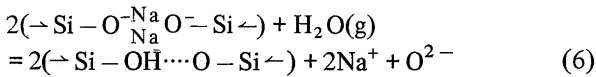
in the acidic composition,

$$\rightarrow Si - O - Si \leftarrow + H_2O(g) = \rightarrow Si - OH/OH - Si \leftarrow \quad (4)$$

in the basic composition,

$$\rightarrow Si - O_{Na}^{Na}O \leftarrow Si \leftarrow + H_2O(g) = \rightarrow Si - O - Si \leftarrow$$
$$+ 2Na^+ + 2OH^- \quad (5)$$

On the other hand, Walsh, Chipman, King and Grant[8] presented another solution mechanism.

in the basic composition

$$2(\rightarrow Si - O_{Na}^{Na}O^- - Si \leftarrow) + H_2O(g)$$
$$= 2(\rightarrow Si - OH \cdots O - Si \leftarrow) + 2Na^+ + O^{2-} \quad (6)$$

in the strong basic composition

$$O^{2-} + H_2O(g) = 2(OH^-) \quad (7)$$

In the acidic glass, water behaves in a similar fashion to basic oxides, that is to say, it reacts with double-bonded oxygen and shows a network-breaking effect. While water reacts as an acid and displays network-linking effect shown in eq. (5). We can conclude from the supposition above described that water plays role as amphoteric material.

Fuwa, Banya, Fukushima and Iguchi[23] studied the change of solubility of water in slag of the CaO-SiO$_2$ system when various sorts of oxide were added. Summarized results are shown in **Fig. 7**. It will be seen that the additive having larger I value such as P_2O_5, B_2O_3 and GeO_2 increases the solubility of water in the acidic composition but, contrary to this, Al_2O_3 and TiO_2 which has

Fig. 8   Relationship between the solubility of water in slag of the CaO-SiO$_2$ system and the Al$_2$O$_3$ content added[23],[24].
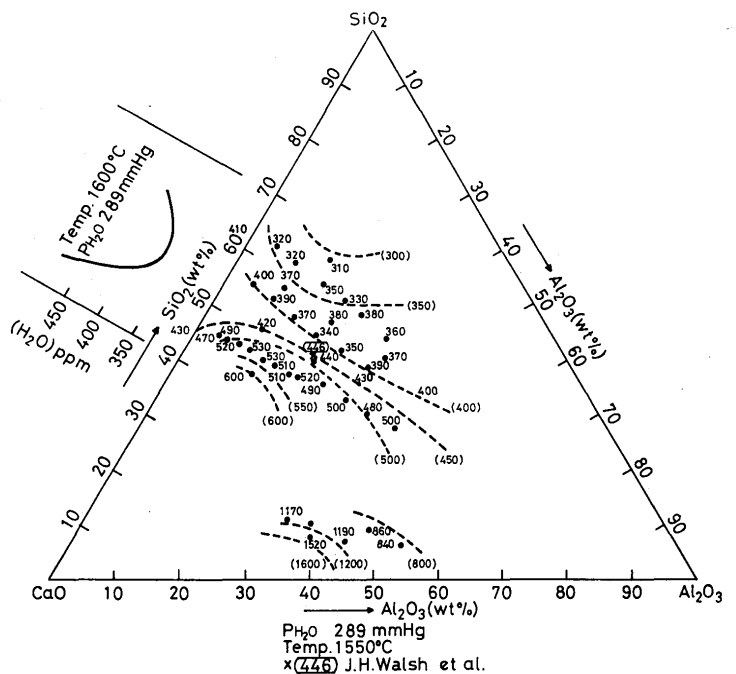
Fig. 9   Solution diagram of water in slag of the CaO-SiO$_2$-Al$_2$O$_3$ system[25].

lower I value decreases. Further, they found the minima of the solubility of water in the CaO-SiO$_2$-Al$_2$O$_3$ system when the following composition, $CaO + AlO_{1.5}/SiO_2 = 1$, was chosen. As shown in **Fig.8**[23],[24], it must noticed that the additive effect of Al_2O_3 on the solubility of water changes depending on the basicity of slag (CaO/SiO$_2$). Still, the explanation of the cause and the additive effect of TiO$_2$ remain unclear.

Iguchi, Banya and Fuwa[25] drew the solution diagram of water in the CaO-SiO$_2$-Al$_2$O$_3$ and CaO-SiO$_2$-TiO$_2$ systems. (**Figs. 9, 10**) In the former case, it was determined that the additive effect of Al_2O_3 differs at the boundary of metasilicate (MO·SiO$_2$). That is, in the acidic composition, the addition of Al_2O_3 decreases the solubility
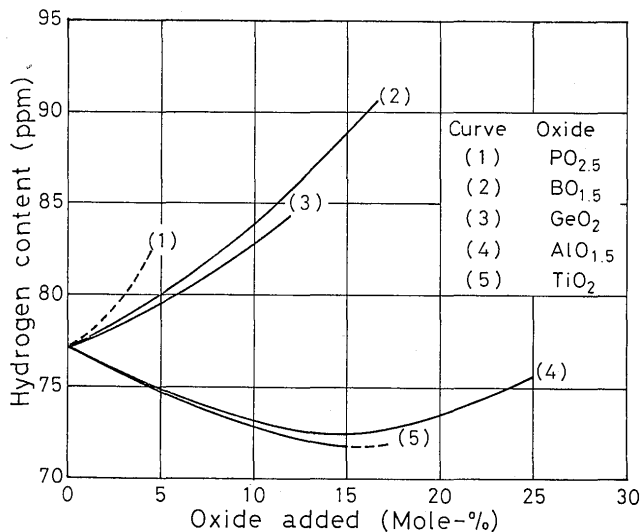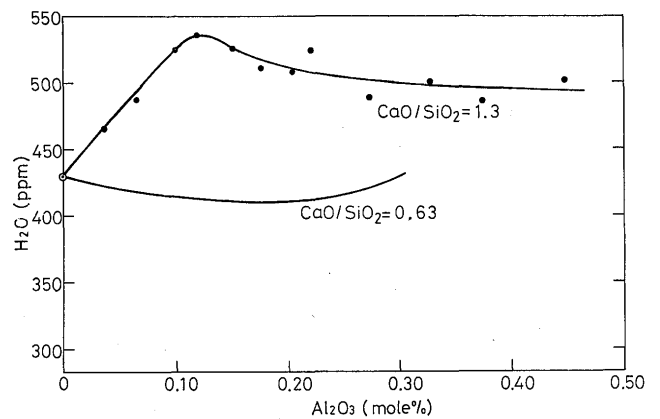

Fig. 7   Change of the solubility of hydrogen in slag of the CaO-SiO$_2$ system when various sorts of oxide were added[23].
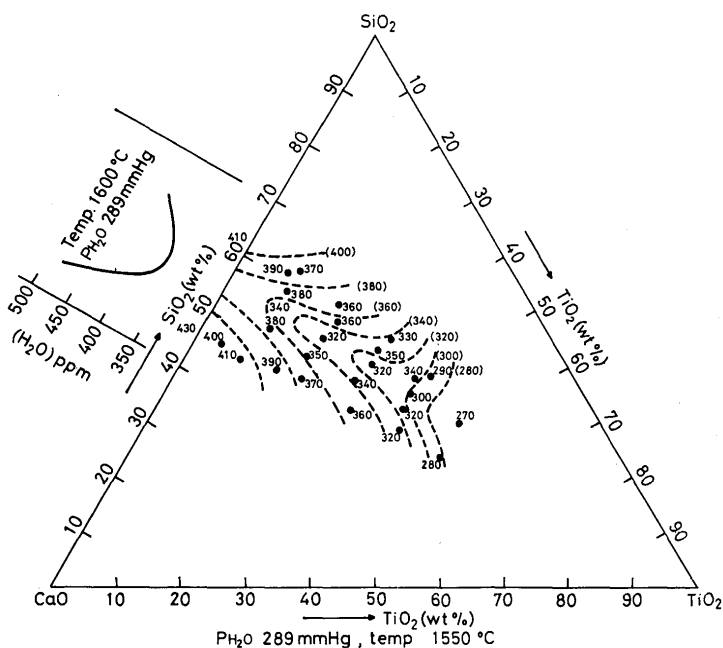
Fig. 10   Solution diagram of water in slag of the CaO-SiO$_2$-TiO$_2$ system[25].
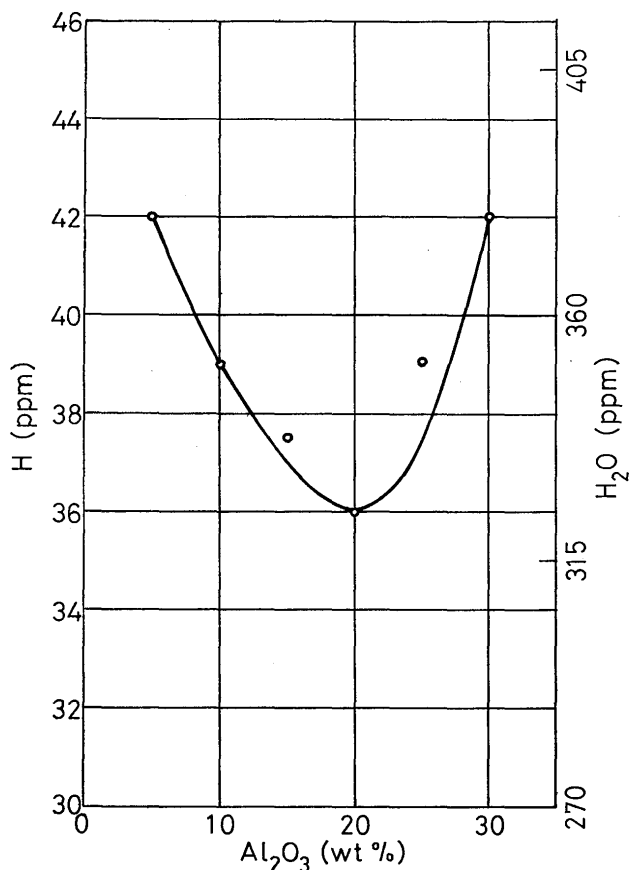

Fig. 11   Relationship between the solubility of water vapor in slag pf the CaO-SiO$_2$-Al$_2$O$_3$ system and the Al$_2$O$_3$ content added[26]. (CaO/Al$_2$O$_3$ = 0.6, Temp. = 1550°C, P$_{H_2O}$ = 190 Torr.)
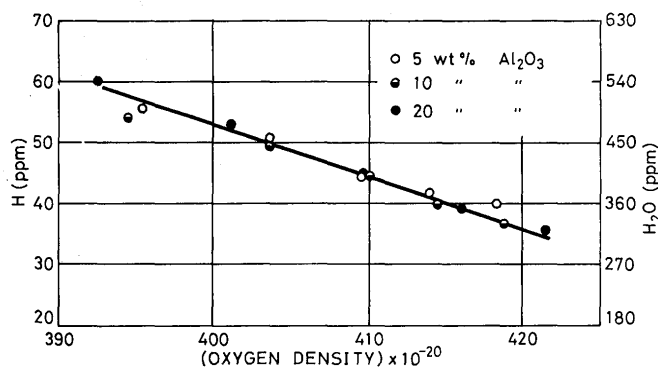

Fig. 12   Relationship between the solubility of water and the oxygen density of slag in the CaO-SiO$_2$-Al$_2$O$_3$ system[26]. (temp. = 1550°C, P$_{H_2O}$ = 190 Torr.)

of water which shows a minimum and then increases by the further addition of Al$_2$O$_3$. Besides, in the basic composition, the addition of Al$_2$O$_3$ increases the solubility of water, which shows a maximum solubility and then shows the tendency to decrease. In the latter case, it will be seen that TiO$_2$ as additive plays only the role of dilution of the solubility of water in the CaO-SiO$_2$ system. Beyond a certain amount of TiO$_2$ added, TiO$_2$ shows amphoteric nature in relation to the CaO-SiO$_2$ system and the minimum solubility disappears with the increase of TiO$_2$ addition.

Sachdev, Majdic and Schenck[26] studied the solubility of water in slag in the CaO-SiO$_2$-Al$_2$O$_3$ system. As shown in Fig. 11, the solubility of water decreases with the addition of Al$_2$O$_3$ and reaches to minimum at 20 wt%. With further addition of Al$_2$O$_3$, the solubility of water conversely increases, the cause was interpreted from the change of coordination number from AlO$_4^{5-}$ to AlO$_6^{9-}$ at 20 wt% Al$_2$O$_3$ addition.

Further, they arranged with the use of oxygen density parameter, which was proposed by Lacy[27], about the relationship between oxygen density value and the solubility of water in slag in the CaO-SiO$_2$-Al$_2$O$_3$ system containing up to 20 wt% Al$_2$O$_3$.

Given the density and composition of a silicate the absolute number of oxygen ions in a c.c. of the solid can be readily calculated, if Avogadro's number and the molecular weight of the constituent oxides be assumed with the following equation.

$$\text{oxygen density} = \rho \cdot L \cdot N_O / \overline{M} \qquad (8)$$

where

ρ = density of the melt in gram per cm^3

L = Avogadro's number

N$_O$ = mole fraction of oxygen atoms in the melt

$\overline{M}$ = average molecular weight of the melt calculated from the molar concentration of each melt component

The oxygen density is a structure parameter because more than 90% of the melt volume is normally occupied by oxygen ions alone, the small cations easily entering into the interstices of the silicate network. As shown in Fig.12[26], the linear relation between the solubility of water and the oxygen density is recognized. It means that the interstices of the silicate network play an important role to accomodate water.

3. Basicity of slag and the solubility of water

The problems as for the solubility of water in oxide melt by many investigators for 30 years were summarized as follows:

(1) The effect on the solubility of water in slag of the CaO-SiO_2 system when contained Al and Ti ion can not be looked as identical.

(2) When the solubility of water was arranged with the simplified basicity of oxide melt (CaO/SiO_2), the occurrence of minimum solubility of water at definite value of CaO/SiO_2 was reported. However, the investigation of all sorts of approaches must be carried out because opposite opinion by Franz and Scholze was presented[9]. It must be considered that there shows no minimum solubility of water at definite CaO/SiO_2 value when Al_2O_3 was added.

(3) Arrangement with the oxygen density must be used.

(4) Although the success to solve the structure change of oxide melt were winned in a few cases with the aid of the solubility of water, the arrangement with newer measures and wider studies are wanted in future.

4. Solubility of nitrogen in oxide melt

Leiby and Chen[28] showed that there occurs solution of nitrogen in glass physically as well as chemically like inert gas.

Mulfinger and Meyer[29] studied the solubility of nitrogen in glass of the $74SiO_2$-$16Na_2O$-$10CaO$ system with vacuum fusion-extraction or with carrier gas method with oxygen blowing, and they obtained nitrogen content of 3.5×10^{-4} Ncm^3/cm^3 glass at 760 Torr which corresponds to about 1/10 of the physical solubility of helium. However, it was proved that ten times solubility could be obtained under particular experimental conditions such as reducing atmosphere, which would form ammonia from nitrogen and gas-flame at high temperature. On the other hand, the solubility of nitrogen becomes thousand times at 1350°C when ammonia gas was blown into the oxide melt.

Kamyshov, Esin and Chuchmarev[30] determined that the solubility of 0.44 wt% occurred in slag of the CaO-

Al_2O_3-SiO_2 system when CO and nitrogen gases were blown into.

Mitchell[31] recognized NH compound with infrared absorption study when ammonia gas was blowed into glass of the Na_2O-B_2O_3 system from that the solution of nitrogen occurs chemically.

Mulfinger and Franz[32] examined the previous reports concerning infrared absoption study, and summarized the wavelength of OH-, NH- and NH_2- band recognizing in various glasses with the change of experimental conditions.
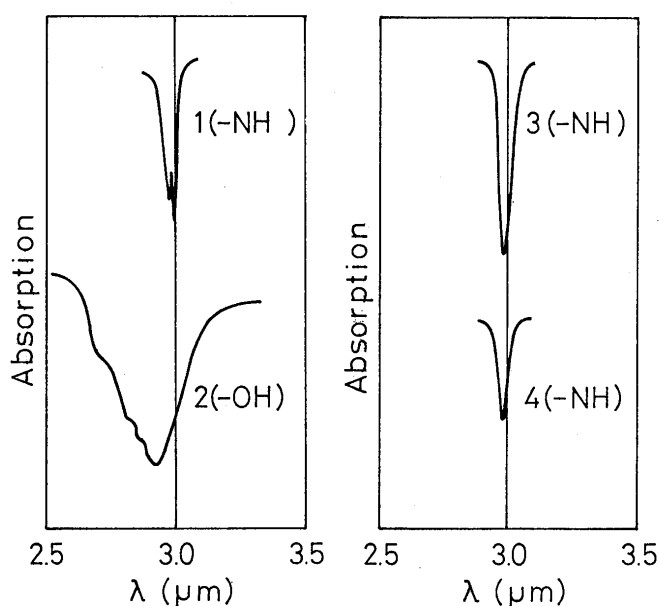

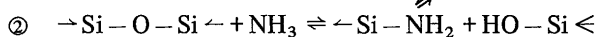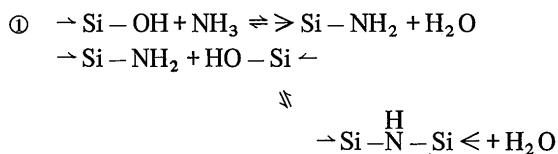Fig. 13　Infrared adsorption bands of -OH and -NH.[33]

Wannagat and Niderprüm[33] studied infrared absorption of organic compound containing silicon, and recogneized the absorption band of OH-, NH- and NH_2- near 3μ. The results are shown in Fig.13. Based on these results, Mulfinger and Franz[32] investigated infrared absorption spectrum occurring at $2 \sim 5\mu$ in glasses of the Na_2O-CaO-SiO_2, Na_2O $2SiO_2$, Na_2O-B_2O_3 and B_2O_3 systems when water vapor, NH_3, H_2O +D_2O, and D_2O vapor and N_2 (dry and wet) was blown into, and summarized as follows:

(1) From the occurrence of NH- band, it was certified that the absorption at 3μ changed to 2.93 or 2.98μ depending on glass composition.

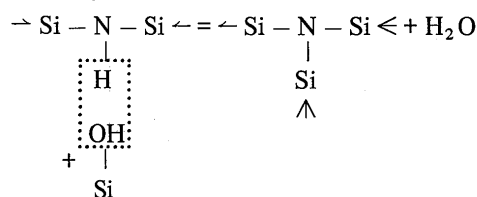(2) The following mechanisms,

$$\to Si - OH + NH_3 \to > SiONH_4$$
$$> B - OH + NH_3 \to > BONH_4$$

were denied from the reason that the absorption bands at 3.19, 3.29 and 3.54μ were not identified in the case of compound containing ammonia.

(3) The following mechanisms were accepted.

① $\rightarrow Si - OH + NH_3 \rightleftharpoons > Si - NH_2 + H_2O$

$\rightarrow Si - NH_2 + HO - Si \leftarrow$

$$\rightarrow Si - \overset{H}{\underset{}{N}} - Si \ll + H_2O$$

② $\rightarrow Si - O - Si \leftarrow + NH_3 \rightleftharpoons \leftarrow Si - NH_2 + HO - Si <$

(4) When a small amount of water are contained, the follwing reaction will be occured.

$$\rightarrow Si - N - Si \leftarrow = \leftarrow Si - N - Si \ll + H_2O$$

$$\begin{array}{cc} H & Si \\ OH & \wedge \\ + & \\ Si & \end{array}$$

Shimoo, Kimura and Kawai[34]~[36] pursued the state of solved nitrogen in slag of the $CaO\text{-}Al_2O_3$ and $CaO\text{-}Al_2O_3\text{-}SiO_2$ systems under the existence of graphite and concluded as follows:

(1) Nitrogen dissolved exists as both CN^- and N^{3+}, but the existence of CN_2^{2-} can not confirm.

(2) The content of CN^- increases with increasing CaO content, and decreases remarkably with increasing SiO_2 content. Structurally, an interesting result is shown in Fig.14, and it will be seen that the solubility
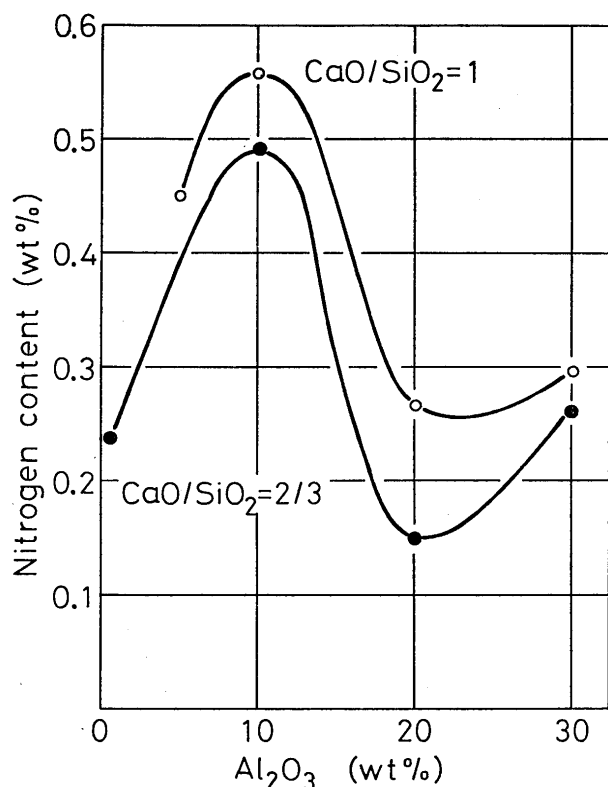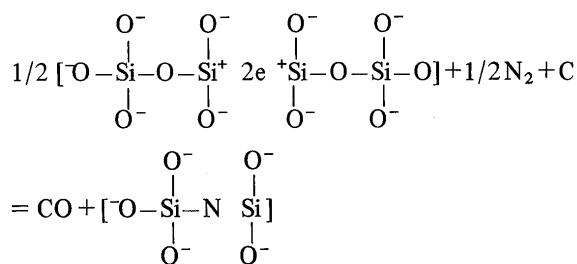

Fig. 14 Relationship between the solubility of nitrogen in slag of the $CaO\text{-}SiO_2\text{-}Al_2O_3$ system and the Al_2O_3 content added[35].

of nitrogen in slag depends on the state of aluminium ion in slag but independ on CaO/SiO_2 ratio.

Davis and Meherali[37] showed that the reducing conditions is necessary to occur the solubility of much nitrogen in slag of the CaO $(MgO)\text{-}Al_2O_3\text{-}SiO_2$ system. In this case, nitrogen can substitute with double-bonded oxygen (O°) as follows:

$$1/2 \, [\overset{O^-}{\underset{O^-}{\overset{|}{\underset{|}{O-Si-O-Si^+}}}} \quad 2e \quad \overset{O^-}{\underset{O^-}{\overset{|}{\underset{|}{^+Si-O-Si-O}}}}] + 1/2 N_2 + C$$

$$= CO + [\overset{O^-}{\underset{O^-}{\overset{|}{\underset{|}{O-Si-N}}}} \quad \overset{O^-}{\underset{O^-}{\overset{|}{\underset{|}{Si}}}}]$$

Choh, Hanaki, Kato and Inoue[38] studied the solubility of nitrogen in slag of the $CaO\text{-}Al_2O_3$ and $CaO\text{-}Al_2O_3\text{-}SiO_2$ systems under the reducing conditions, and concluded that nitrogen in slag takes the form as N^{3-} and CN^- and the amounts depend on P_{CO}.

5. Summary

In this report the author summarized the relation between the solubility characteristics of water vapor and nitrogen and slag composition from the standpoint of structural study on slag. From this, it was shown that strong correlation is found between the state of aluminium ion in slag and the solubility of gas. However, an important problem as for the role of titanium ion in slag has been left as unresolved problem.

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