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Structure of Slag (Ⅲ) [†]
—Structural problems on slag—

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Abstract

The historical development of structural theories of oxide melt is given. Also many problems in chemical welding are discussed form the standpoint of structure of slag.

1. Historical review on the structure theories of slag

1.1 Molecular theory [1)-3)]

The basic concept of this theory is that many complex compounds in molten slag by the analogy with the fact that we can observe the formation of various compounds in solidified slag. Schenck thought that the following stable compounds such as $(FeO)_2 SiO_2$, $(MnO)_2 SiO_2$, $CaO.SiO_2$, $(CaO)_4 P_2 O_5$ and $(CaO)_3 \cdot Fe_3 O_4$ are formed in molten slag.

Thus, the following dissociating reactions are given.

$$(FeO)_2 SiO_2 = 2FeO + SiO_2 \tag{1}$$

$$Fe + (CaO)_3 Fe_3 O_4 = 3CaO + 4FeO \tag{2}$$
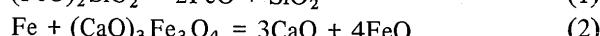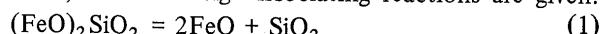
In this theory, it is important to know total content of iron (%ΣFe), and this can be obtained from free FeO, $(FeO)_2 SiO_2$, and $(CaO)_3 Fe_3 O_4$. Accordingly,

$$(\%\Sigma Fe) = 0.78 \ (\%FeO) + (\%Fe)_{CaO} + (\%Fe)_{SiO_2} \tag{3}$$
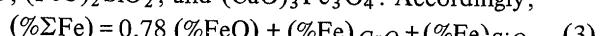
By combining this equation with the relation for dissociation coefficient and temperature, (%ΣFe) can be calculated from the isolated components determined by chemical analysis of slag. Although great success was achieved in the ferrous as well as non-ferrous fields with the use of this theory, it is now considered to be a conventional thought.

1.2 Ionic theory

With the development of electrochemical and thermodynamical studies of slag in recent years, it became sure that molten slag is not composed of neutral assemblage, but dissociates to ionic species. In Table 1,[4)] electrical conductivities of various substances are compared. It will be seen that molten slag shows similar electrical property with ionic materials.

From X-ray diffraction studies, it became clear that Si—O bonds take chain- or ring-structure in the silicate minerals or glasses as shown in Fig. 1.

In general, basic components such as $Na_2 O$,

Table 1. Electrical conductivities of various substances above the melting point[4)]

System	$\dfrac{\chi \ (\text{above m.p.})}{\chi \ (\text{below m.p.})}$	Characteristic
NaCl $CdCl_2$ AgCl	3×10^3 2×10^2 3×10	typical ionic conduction
Hg Pb	0.2 0.5	typical electronic conduction
1/1 $CaO\text{-}SiO_2$ 1/1 $MnO\text{-}SiO_2$	2×10^2 3×10^2	ionic conduction
$Al_2 O_3\text{-}SiO_2$ (0.08 mol $Al_2 O_3$)	1	probably ionic conduction

$$SiO_4^{4-} \qquad Si_2 O_7^{6-} \qquad Si_4 O_{12}^{8-}$$
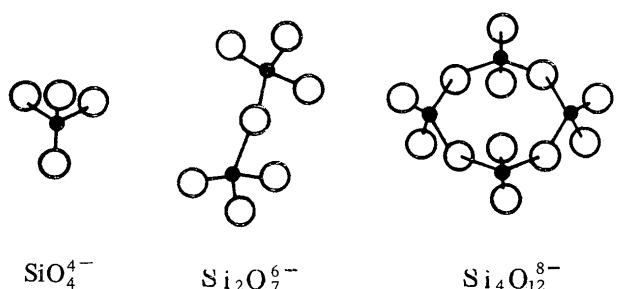
Fig. 1　Various forms of silicate anion

CaO,MnO,MgO and FeO ionize to cation and anion (O^{2-}) in slag and act to form complex anions according to the following reactions.

$$SiO_2 + 2O^{2-} = SiO_4^{4-} \tag{4}$$

$$2SiO_4^{4-} = Si_2O_7^{6-} + + O^{2-} \tag{5}$$
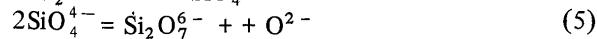
In Fig. 1, some examples of the simple anions are shown.

1.2.1 The first experimental proof

Endel and Hellbrügge measured the viscosity of the systems, $R_2O–SiO_2$, $RO–SiO_2$ and $M_mN_n–SiO_2$(M indicates cation of tri- or quatre-valency) in 1940–41.[5),6)] They summarized the effect of ionic radii and valency of cation on viscosity and discussed the structural change of silicate. As an example, viscosity change with the increase of ion content of alkaline metals is shown in Fig. 2. The result on the specific resistivity showed similar tendency and structural change takes place between 1/1 and 2/1 of cationic molar ratio. In

Table 2, structural changes of silicate anions with increasing content of basic component are shown. They

Table 2. The network theory of liquid silicate suructure[5),6)]

| Equation	Si/o ratio	Silicate entities	η (poise) at 1400°C
SiO_2	$(Si_8O_{16})^0$	Continuous three-dimensional network	10^{10}
$Na_2O \cdot 2SiO_2$	$(Si_8O_{20})^8$	'infinite 'two-dimensional sheets	280
$Na_2O \cdot SiO_2$	$(Si_8O_{24})^{16}$	Simple tetrahedral which own jointly a edge	1.6
$2Na_2O \cdot SiO_2$	$(Si_8O_{32})^{32}$	SiO_4^{4-}	<1
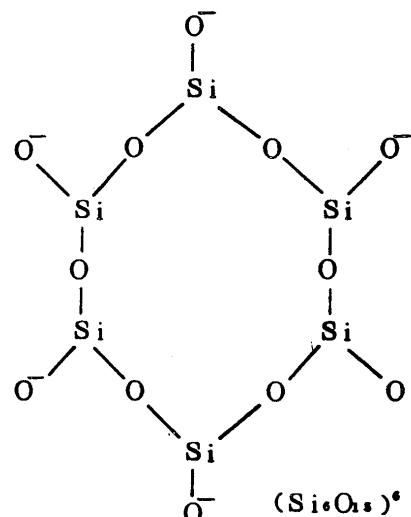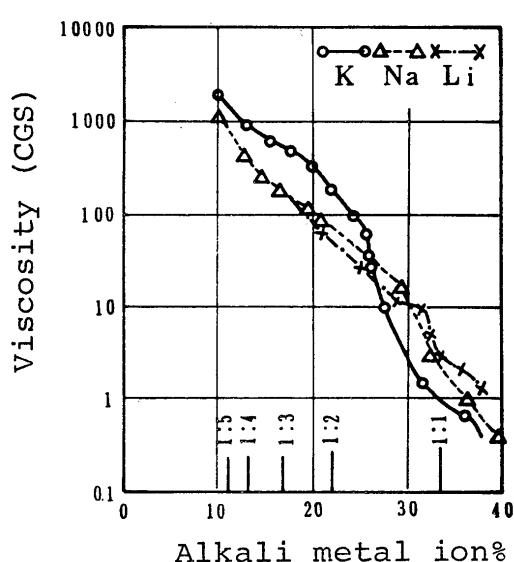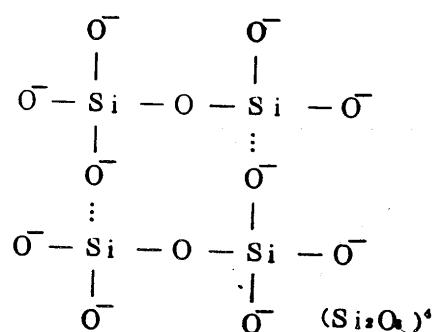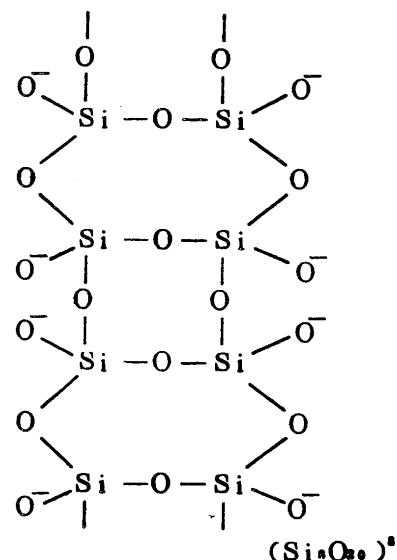
Fig. 2   Effect of alkali-metal oxides added on the viscosity of silicate[4), 5)]

Fig. 3   Various forms of silicate anion proposed to inter-plet viscosity change[4), 5)]
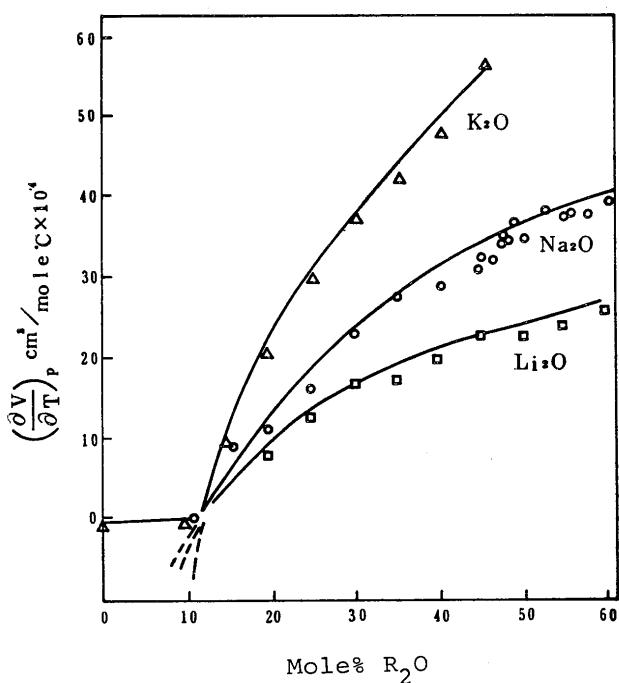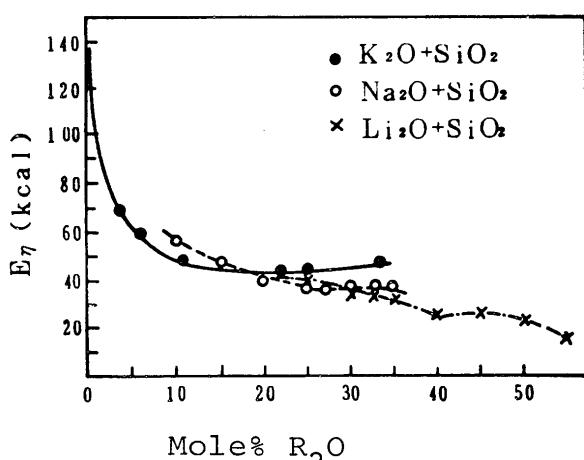
thought that silicate takes two-dimensional structure at the composition of $R_2O/SiO_2=1/2$, but it changes to simple chain-like structure at the composition of 1/1. Their models of silicate anions are shown in Fig. 3.

1.2.2 The second experimental proof

The studies of silicate structure have been continuously published by Bockris' school since 1952. [7]-[14] As an example, thermal expansion coefficient[12] and activation energy of viscosity[13] with the change of basic content are shown in Figs. 4 and 5. They certified that structural change occurred within the range of 10–20 mole% of R_2O or RO added and showed disagreement to the result by Endell and Hellbrügge[5],[6] that is to say, there was no change near $R_2O/SiO_2=1/1$. From these evidences, they explained that structural change is attributed to the breakdown of network of relatively large three-dimensional bonding up to 10 mole% R_2O. The experimental equations of various silicate anions having Si/O ratio from 0.25 to 0.33 are given in Table 3. Three-or four-membered ring structure shown in Figs. 6(a) and (b) must be formed when RO content becomes near 50%(Si/O=1/3). In the former case, angle of Si-O-Si becomes 133°. In the latter case, the angle becomes 145°. The model seems reasonable because the angle of natural silicates is similar to these values. By increasing SiO_2 content, dimer, composed of a pair of three-or four-membered rings, is formed as shown in Figs. 6(c) and (d). In the above discrete theory, the change of physical properties at 10% R_2O can be interpleted from the reason that the length of network becomes longer by structural instability with increasing SiO_2.

However, this theory has two weak points. The first

Fig. 4   Thermal expansion coefficient of the system R_2O-SiO_2[12]

Fig. 5   Change of activation energy of viscosity of the system R_2O-SiO_2[13]

Table 3   Formulae of silicate chain anions in the range Si/O=0.25 to Si/O=0.33

$CaO : SiO_2$	Si : O	Percent molar oxide	Length of chain	Empirical formula
$2CaO : SiO_2$	1 : 4	66	1	SiO_4^{4-}
$3CaO : 2SiO_2$	2 : 7	60	2	SiO_7^{6-}
$4CaO : 3SiO_2$	3 : 10	57	3	$Si_3O_{10}^{8-}$
$5CaO : 4SiO_2$	4 : 13	55	4	$Si_4O_{13}^{10-}$
$6CaO : 6SiO_2$	5 : 16	54	6	$Si_5O_{16}^{12-}$
$11CaO : 10SiO_2$	10 : 31	52	10	$Si_{10}O_{31}^{22-}$
$CaO : SiO_2$	1 : 3	50	∞	$Si_nO_{3n}^{2n-}$
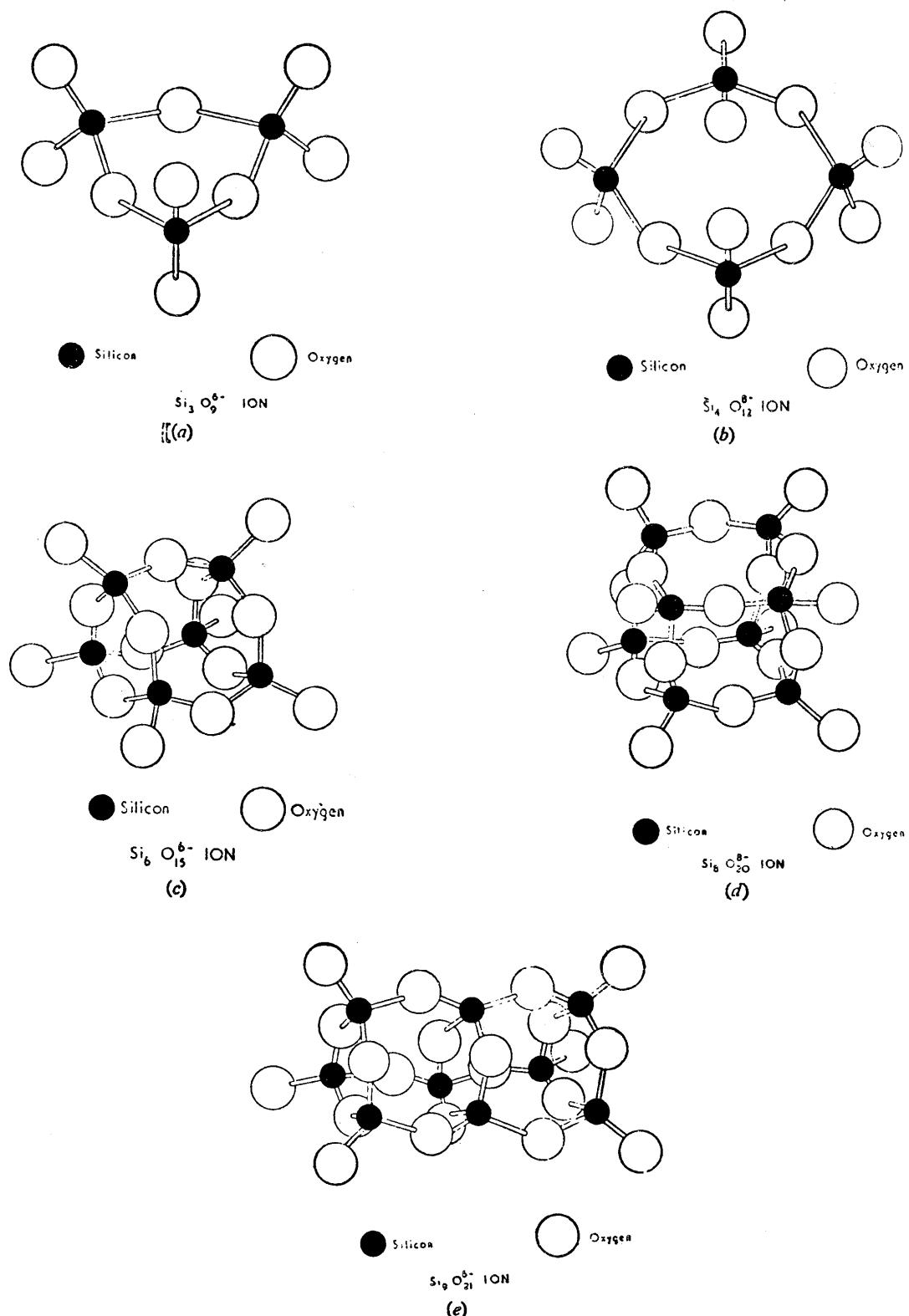
Fig. 6   Discrete anion model[10]

is that the theory can not explain the reason why partial molar volume is held constant in the range of 10% to 33% R_2O. The second is that this theory can not illustrate what structural change occurs when R_2O content exceeds Si/O=1/4. Bockris suggested that diffusion experiment of oxygen ion in slag and X-ray diffraction study are necessitated in determining which is better model, discrete or iceberg model[13].

1.2.3. Proposal by Frohberg

Frohberg reexamined the previous ionic theories of slag, and concluded that structural change of silicate anion does not occur in the range of 10 to 50% for R_2O and 20 to 50% for RO addiiton.[15] When slag changes from basic to acidic composition, he said that the following reactions should be considered.

$$2SiO_4^{4-} = SiO_7^{6-} + O^{2-} \qquad (6)$$
$$Si_2O_7^{6-} + SiO_4^{4-} = Si_3O_{10}^{8-} + O^{2-} \qquad (7)$$
$$Si_3O_{10}^{8-} = Si_2O_9^{6-} + O^{2-} \qquad (8)$$
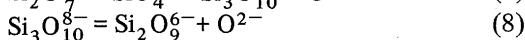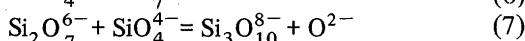
Accordingly, he thought the formation of free oxygen ion in slag and that theories by Herashimenko and Speight,[16] and Richardson[17] are correct. Further, he summarized the reported basicity of slag and defined the oxygen ion concentration in slag[18]. In Table 4, the structural change of silicate anion is summarized.

1.2.4. , Proposal by Toop and Samis

They extended the polymerization theory of silicate anion from binary to thernary system[19]. At first, they obtained equilibrium constant from the equation given by Fincham and Richardson[20].

$$2O^- = O^\circ + O^{2-}, \qquad (9)$$

then

$$K = (O^\circ)\cdot(O^{2-}) / (O^-)^2 .. \qquad (10)$$

From charge balance,

$$2(O^\circ) + (O^-) = 4N_{SiO_2} \qquad (11)$$

is obtained, and the next equation is derived.

$$(O^\circ) = [4N_{SiO_2} - (O^-)] / 2 \qquad (12)$$

On the other hand, from mass balance,

$$(O^{2-}) = (1 - N_{SiO_2}) - (O^-) / 2 =$$
$$= [2 - 2N_{SiO_2} - (O^-)] /2 \qquad (13)$$

is obtained.

Summarizing the above equations, next equation is obtained.

$$4K = [4N_{SiO_2} - (O^-)] [2 - 2N_{SiO_2}$$
$$- (O^-)] / (O^-)^2 \qquad (14)$$

If the values, K and N_{SiO_2} are known, (O^-) can be calculated. Relationship between these values are shown in Fig. 7. Further they noticed the similar behaviour of (O^-) content and free energy of mixing. From the next equation

Table 4 Structure of silicate anion[15]

| Mole%RO added	Structure	Remark
0	"Infinite" three-dimensional network, there is a chance braking to SiO_2 molecules thermally	
0 - (10~20)	Distorted network, with number of broken bonds equal to number of added Oxygen atoms	R_2O-SiO_2, 10-12% RO-SiO_2, 10-20%
(10~20)-33	Complex polymerized rings $[Si_{3n}O_{6n+3}]^{6-}$, $[Si_{4n}O_{8n+4}]^{8-}$	
33 - 50	Simpler polymerized forms above described	Highly, 2~3
50 - 67	Mixture of short chain, $[Si_nO_{3n+1}]^{(2n+2)-}$, (in this case n $\leqslant$ 3) and simple ring	
67 - 70	Further braking to simple tetrahedra proceeds	
70 - 100	SiO_4^{4-}	
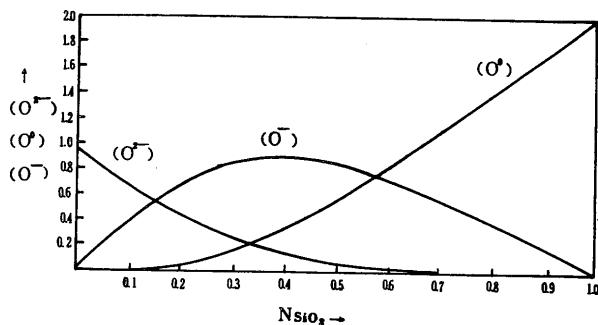
Fig. 7   Equilibrium values of (O°), (O^-), and (O^{2-}) vs N_{SiO_2} for K=0.06 [19]

Table 5   Equilibrium constant K of various binary systems[19]

| System	K	Component	Melting Point(°C)
Cu_2O-SiO_2	0.35	0	1100
$FeO-SiO_2$	0.17	1	1600
$ZnO-SiO_2$	0.06	1	1300
$PbO-SiO_2$	0.04	2	1100
$CaO-SiO_2$	0.0017	2	1600

$$\Delta G_{mix}/4.575T = [(O^-) / 2] \cdot \log K, \qquad (15)$$

we can find a suitable K value which can be derived by the agreement of the experimental and calculated values of free energy. In Table 5, the most desirable values of K for various binary systems are given.

1.2.5. Proposal by Masson

Masson[21] treated the distribution of complex anions in terms of ion fraction, and this treatment differed from that of Toop and Samis.[9] However, this theory is limited to the silicate anion that has no ring structure as in the previous theory,[19]

The following polymerization equations were proposed.

$$SiO_4^{4-} + SiO_4^{4-} = Si_2O_7^{6-} + O^{2-} (K_{1,1}) \qquad (16)$$
$$+ Si_2O_7^{6-} = Si_3O_{10}^{8-} + O^{2-} (K_{1,2}) \qquad (17)$$
$$+ Si_3O_{10}^{8-} = Si_4O_{13}^{10-} + O^{2-} (K_{1,3}) \qquad (18)$$
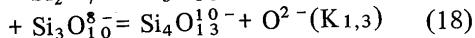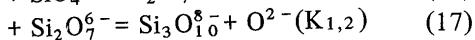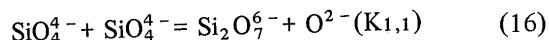
etc.

From these equations,

$$N_{Si_2O_7} = (K_{1,1} \cdot N_{SiO_4}/N_O^{2-}) N_{SiO_4} \qquad (19)$$

and so on.

From the relation,

$$K_{1,1} = K_{1,2} = K_{1,3} = \cdots \cdots = K, \qquad (20)$$

$$\Sigma N_{silicate} = N_{SiO_4} + N_{Si_2O_7} + N_{Si_3O_{10}} + \cdots$$
$$= N_{SiO_4} + (K \cdot N_{SiO_4} / N_O^{2-}) \Sigma N \text{ silicate}$$

$$(21)$$

is obtained.

Rearranging each equations, the final relation,

$$N_{SiO_4} = 1 - N_{O^{2-}}/1 + K(1/N_{O^{2-}} - 1), \qquad (22)$$

is obtained.

Ir the value of K is known for binary systems, N_{SiO_4} is given as a fuction of N_O^{2-}. As an example, theoretical curves of various silicate anions as fuctions of N_O^{2-} for K=1 is shown in Fig. 8.
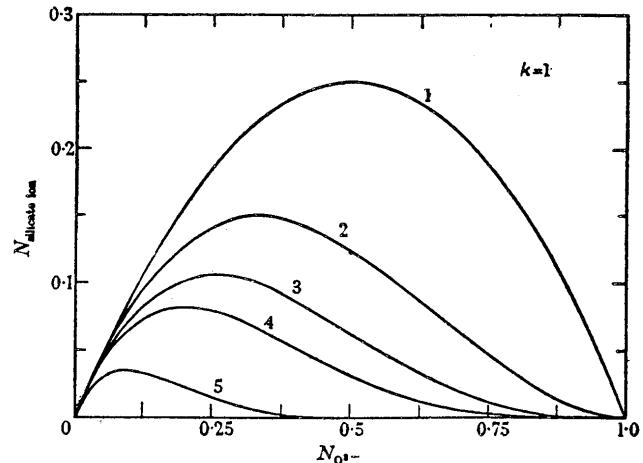

Fig. 8   Theoretical curves of (1) N_{SiO_4}, (2) $N_{Si_2O_7}$, (3) $N_{Si_3O_{10}}$, (4) $N_{Si_4O_{12}}$, (5) $N_{Si_{10}O_{31}}$, as fuctions of N_O^{2-} for K = 1[21]

Further Whiteway and Masson[22] reexamined the polymer theory by Flory.[23],[24] Masson, Smith and Whiteway[25].[26] derived the following useful expression to solve distribution of various silicate anions.

$$N_x = (3x)! / (2x + 1)! \times \left\{ \cfrac{1}{1 + \cfrac{3 a_{MO}}{K_{1,1}(1 - a_{MO})}} \right\}^{x-1}$$
$$\times \left\{ \cfrac{1}{1 + \cfrac{K_{1,1}(1 - a_{MO})}{3a_{MO}}} \right\}^{2x+1} \times (1 - a_{MO})$$

$$(23)$$

In Fig. 9, ion fractions of various silicate anions in the system $FeO-SiO_2$ at 1530-1680°K are shown.

1.2.6. Other proposals

Kapoor and Frohberg[27] presented an equation to get distribution of silicate anion in slag, but the result obtained differs from the result by Masson[26] although the equation is like the one by Toop and Samis.[18]

Yokokawa and Niwa introduced partition fuction based on the assumption that enthalpy change is independent of the composition and showed a good agreement between experimental value and calculated value of activity and free energy of mixing in binary and ternary systems.[29]

1.2.7. Summary

As metioned before, many theories concerning

structure of slag were proposed. Among them, the theory by Lacy is unique in the points that he proposed term of oxygen density and showed the existence of AlO_5.[30)-33)]
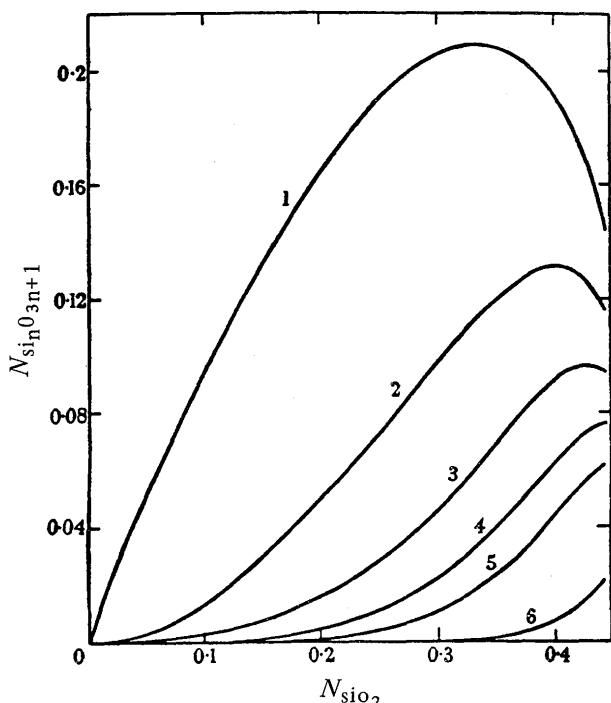

Fig. 9   Ion fractions of SiO_4^{4-}, $Si_2O_7^{6-}$, $Si_3O_{10}^{8-}$, $Si_4O_{13}^{10-}$, $Si_5O_{16}^{12-}$, and $Si_{10}O_{31}^{22-}$ plotted against mole fraction of silica for the system 'FeO–SiO$_2$' at 1530–1680°K[25)]

2. Problems on structural studies of melt

To study the structure of melt, there are many different ways such as electrical resistivity,[4)] thermo-electrical motive force,[34)] electrochemical study,[35)] viscosity,[10)] density,[12)] depression of the melting point,[36)] gas absorption[37)-8,40)] and so on.

However, most of reports discussed structure of melt from the standpoint of phase diagram of the system.

2.1. X-ray and neutron analysis

To know the information of structure by X-ray or neutron diffraction is the dynamical and effective means at present. Many experimentations with diffraction study have been carried out on liquid metals, but studies on molten oxide are limited. In this report, the author discusses the reasons why this field of research is difficult.

2.2. Historical review of diffraction methods

Zarzyski transmitted X-ray to molten salt which is held in the slit with sample holder that can be heated.[41);42)]

Furukawa applied X-ray to the free surface of molten slag that over-flows always from the sample holder.[43)]

Recently, θ–θ method is usually used in which detector and X-ray tube rotate synchronously around sample holder where molten specimen is held.

On the other hand, vertical sample holder that enables heating is recommended, but there are difficult problems to maintain thin window film safely at high temperature.[44)]

In the case of liquid metal, the use of alumina crucible is possible. However, it is difficult to find good material which is useful for purpose to have good corrosion resistence.

In the case of free surface method, surface tension of molten specimen becomes a problem from a demand to get wider free surface.[45)] This problem can be solved by making molten area larger, but it has a limitation.

The author tried to study PbO–SiO$_2$ melt with the crucible of Pt-20%Rh of 12mm square, but the experiment failed due to reaction. The experiment in CaO–SiO$_2$ system was not in success due to low surface tension. From these point of view, it is necessitated to pay attension to the wetting property of melt to crucible. Until now, only the system PbO–B$_2$O$_3$ by Furukawa is successfully studied.[43)]

Neutron diffraction study has many advantages when compared with X-ray study. This method corresponds to vertical crucible method because we utilize intensive transmittant ability. However, there remains some problem to exclude the effect of crucible.

18,2.3. Neutron magnetic resonance study

When specimen was laid in magnetic field, there occurs the change of energy state of molecule, atom or atomic neucleus. The change depends not only on magnetic field applied, but also on the internal field of specimen and on the chemical bond and molecular motion. Thus we can observe phenomenon named as chemical shift because resonanse energy changes minutely by the difference of outer electron and the screening effect. Although there are effective species such as fluorine, aluminium or sodium which has higher isotope ratio, there is no report that obtained useful information on molten state.

2.4. Optical absorption study

There is only a paper on molten salt by infrared absorption study.[46)] It would be necessary to investigate structure of molten oxide with the means such as ultraviolet, visible, infrared, far-infrared and Raman absorptions.

2.5. Study of dielectric moment

With the difference of structure, the resonating value of slag changes with the change of frequency. With regards to molten material having ionic conductivity, it becomes difficult to interplet the result. Until now , result on B_2O_3 melt was only published.[47]

2.3. Summary

In spite of necessity of studying the molten state, it is difficult to do so because there are many problems concerning corrosiveness and elecrical conduction of sample holer.

3. Problems on getting glassy materials by quenching

Glasshy material is usually obtained from molten state by quenching to room temperature and various physical techniques are applied to know the structure.

Since old time, it has become practical wisdom to obtain solid slag which is quenched from molten state into water. According to modern knowledge, velocity of water quenching is very slow and changes its structure. It is a great matter of concern whether the state of liquid can be brought to room temperature without change of the structure or not. The amorphous state can be observed for the quenched slag by X-ray analysis, but the nature of the amorphous state is not clear.[48]

In the field of liquid metal, the principle named levitation has been developed.[49] The floating molten metal is dropped onto water-cooled copper plate and striked by a hammer.[50] This method can not be applied to oxide melt quenching because oxide melt can not float and frequently has high viscosity. In U.S.A., the techniques which extrude molten sample from the hole of crucible bottom by blanc shot[51] or by braking diaphram with high pressured gas[52] have been developed to molten metal quenching. As for the application of this technique to oxide melt, only a paper has been published in U.S.A.[53] It is important to pay attention to obtain glassy materials containing transition metal ion because the valency of ion depends on quenching velocity.

4. Application of various analysis to solidified specimen

Excellent analyses that we must deal with are as follows: The first is a paper by Lentz.[54] The second is the determination of phosphate compounds by Richardson,[55] and the third is the determination of silicate anions by Masson et al..[56]

4.1. Analysis by gas-chromatography or high resolution mass anlyzer

Lentz[54] found that the following reactions occur in silicate, for example in Mg_2SiO_4,

$$Mg_2SiO_4 + 4HCl \rightarrow H_2SiO_4 + 2MgCl_2 \quad (24)$$
$$H_2SiO_4 + 4(CH_3)_3SiCl \rightarrow$$
$$[(CH_3)_3Si]_4SiO_4 + 4HCl \quad (25)$$
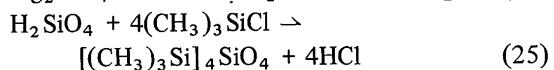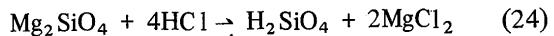
He used natural olivin, sodalite and natrolite as standards, and determined SiO_4^{4-}, $Si_2O_7^{6-}$, and $Si_3O_{10}^{8-}$ species respectively. Then, he succeeded in determining the amounts of various silicate anions in sodium silicate by gas chromatography.[56]

Götz et al. have applied this method to $PbO-SiO_2$ glasses, and obtained gas chromatograms at various temperatures as shown in Fig. 10, and determined the
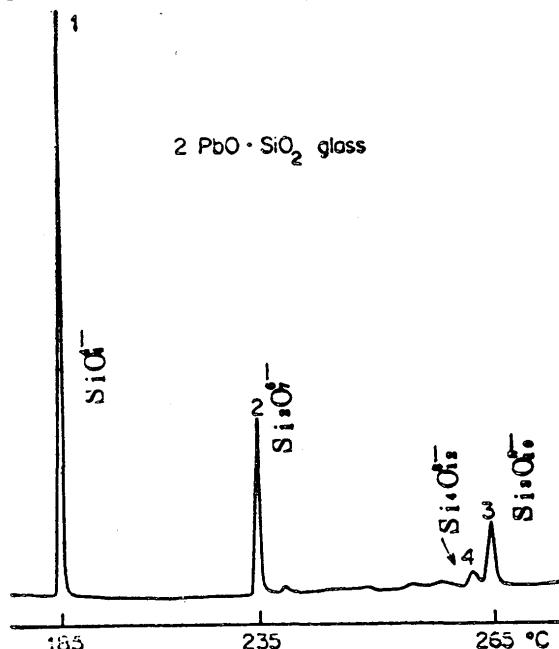

Fig. 10   Chromatographic pattern for lead orthosilicate glass[28]

existing silicate anions percentages.[56] However, one should note that SiO_4^{4-}, anion is easily polymerized to $Si_2O_7^{6}$, anion when the holding time is changed from 1 to 20 hrs at the crystallization temperature of 500°C. This tendency is shown in Fig. 11. The result agrees
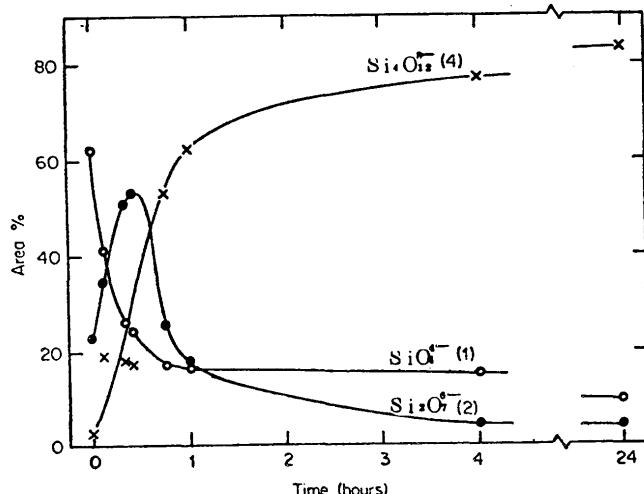

Fig. 11   Change in constitution of lead orthosilicate glass on crystallization at 500°C.[57]
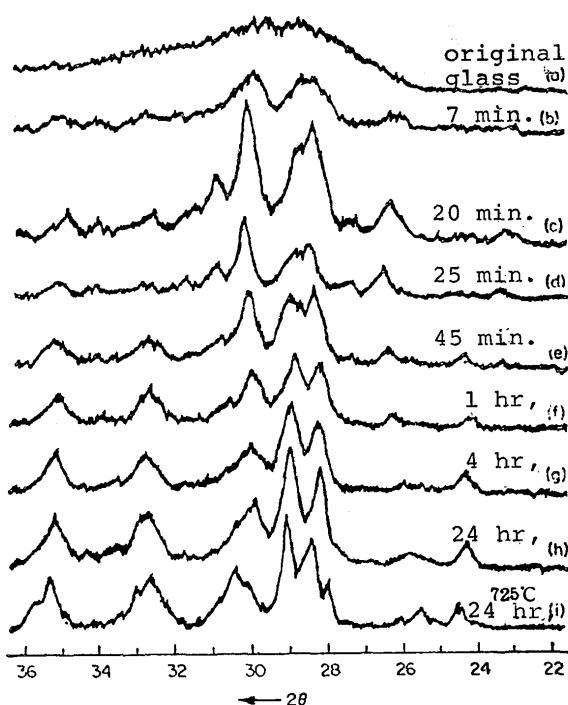
Fig. 12   Diffractometer chart sections for $2PbO \cdot SiO_2$ after crystallization at 500°C for various times[57]

with the diffraction results shown in Fig. 12. It must be noticed how we choose solidifying velocity to obtain glassy material.[57),58]

4.2. X-ray diffraction studies

Warren et al. performed X-ray diffraction analysis for various sorts of glasses.[59)-61] Zernicke and Prins showed that analytical method on mono-atomic liquid can be applied to glasses composed of atoms more than two.[62] From this analysis, they proved that random network theory presented by Zachariasen [63] is a correct model. In this stage, X-ray powder camera method was used, but, recently, Warren reexamined the result by new techniques using high accuracy X-ray instrument and monochrometer to SiO_2.[64]

The accuracy of X-ray analysis depends on the following items.

1) the effect of termination effect[65]
2) the effect of normalization procedure[66]

Although x-ray (neutron, electron) analysis gives an exact information on inter-atomic distance, it gives less information for the co-ordination number when an atom was noted in liquid specimen.

4.3 Study by NMR(nuclear magnetic resonance)

Bray et al. paid attention to the uncertainty of behaviour of boron ion in glasses.[67)-70] They performed NMR studies on compounds containing boron, the specimens composed of B_2O_3 and other oxides, which were fused and cast into carbon mould. From these studies, they concluded that resonance occuring at

27.6Mc is attributed to 3-coordinated boron and the one at 570Mc is to 4-coordinated boron. Bray et al. carried out the detailed study on the system $PbO-B_2O_3$ and found that the chemical shift of Pb^{207} occurs with the decrease of ionicity of Pb—O bond with increasing PbO content from the comparison with phase diagram,[71] thermal expansion,[72] infrared absorpiton,[73] and X-ray studies.[43] Furthermore, it was determined that the chemical shift of Pb^{207} in the system $PbO-SiO_2$ showed only 8 gauss when compared with the shift of 23 gauss on the system $PbO-B_2O_3$. They concluded that glass of the system $PbO-SiO_2$ has slightly random network structure and similar condition of the bond between crystalline and glassy materials.

4.4 Structural study from emission X-ray peak shift

As discussed in the previous review,[74] the role of aluminium or titanium ion in glass is unclear and the contribution to the basicity of slag or glass should be clarified in future.[75]

The authors have tried to solve the behaviour of various ions in slag or glass with emission X-ray peak shift study.[76)-78]

Dodd et al. studied peak shift of various ions from the standpoint of chemical bond. As examples, peak shifts of $Si-K_\beta$ and $Al-K_\beta$ of various compounds are shown in Figs. 13 and 14.[79]

According to our experiment, peak shift of silicate glasses is not remarkable and our interest is on the occurrence of X-ray satellite.

4.5. Infrared absorption studies

Infrared absorption studies on natural silicates were carried out by Milky[80] and Saksena.[81] Simons et al. studied the absorption behaviours of quartz, cristoblite and tridymite, and therefrom developed the study to binary silicate glasses.[82),83] Afterwards, many investigations as for R_2O-SiO_2 and $RO-SiO_2$ systems were done.[84),85]

In Japan, the systematic study ranging over wide compositions were carried out by Yanagase and Suginohara.[86]

4.6. Study by ESCA (electron spectroscopy for the chemical analysis)

When X-ray, ultra-violet, electromagnetic rays or charged particle strikes specimen, electrons are emitted from the surface. From the energy measurement, we can obtain the information for the energy level of molecule or atoms of specimen. This method is named as ESCA. The results of glassy material of the system $PbO-SiO_2$ were already published.[78] Although it will be understood that the energy level of oxygen atom is considerably different for different specimens, it is questionable whether this method can be applicable to solve various indistinct problems or not.
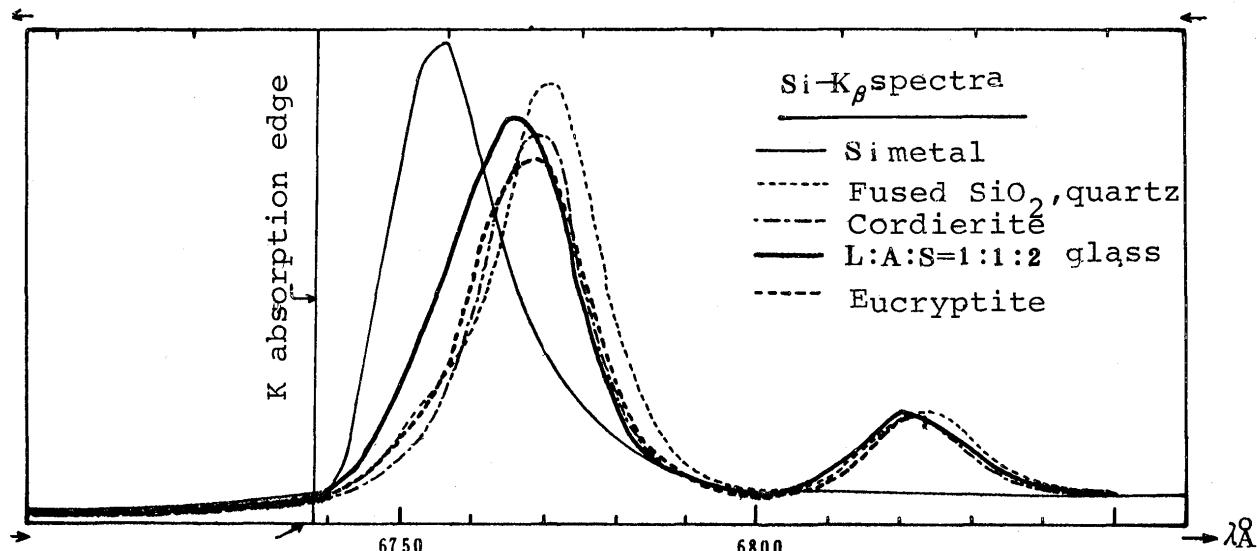
Fig. 13 SiK_α emission spectra of LAS glass and high–quartz
phase crystal of same composition with reference
spectra[79]
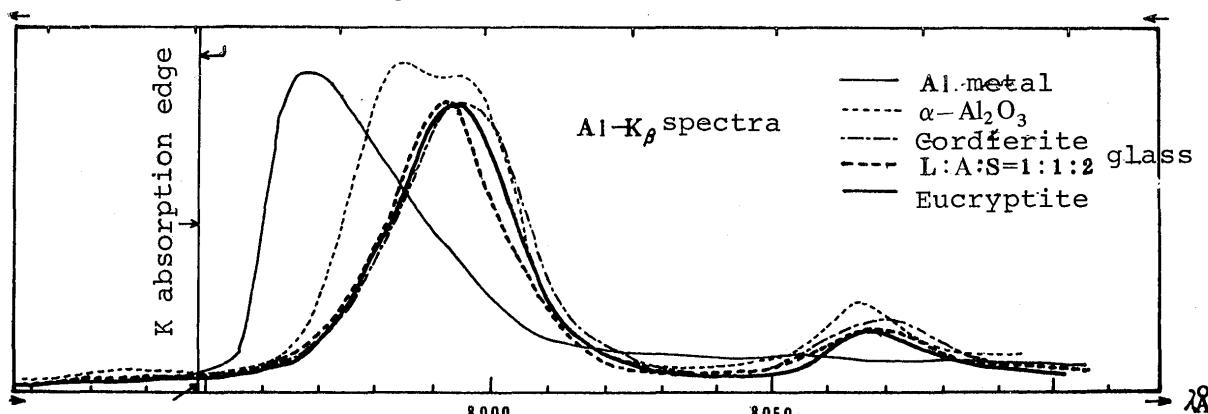
Fig. 14 AlK_α emission spectra of LAS glass and high–quartz
phase crystal of same composition with reference
spectra[79]

4.7. Other methods

In order to study the structure of oxide melt, it is necessary to know interatomic distance, that is to say, coordination number around an atom noticed. To obtain such information, there are further techniques, such as measurement of magnetic property when specimen shows magnetic behaviour, optical absorption study beyond infrared, the measurement of molar refractivity and so on.

5. Conclusion

In this discussion, the author summarized historical review concerning the structure of oxide melt, Masson et al. reported the powerful evidence of the distribution of various complex silicate anions although their proposal is based on many assumptions. There are many questionable points whether the structure of molten oxide can be brought to room temperature without structural change. Previously, we showed the possibility of precipitation of fine crystallites from X-ray small angle scattering and electron microscope studies.[78] It remains unclear what is amorphous state. Summarized studies with physical and chemical methods are desired to solve the structure of oxide melt, particularly, on the molten state.

References

1) H. Schenck: Arch. Eisenhuttenw., 1 (1928), p.483.
2) H. Schenck: "Physik. Chem. Eisenhuttenproz." (1935), BD.II Springer, Berlin.
3) H. Schenck and W. Rie: Arch. Eisenhuttenw., 9 (1936), p.589.
4) J. O'M. Bockris, J. A. Kitchener, S. Ignatowitz and J. W. Tomlinson: Disc. Faraday Soc., (1948), p.273.
5) H. Hellbrugge and K. Endell: Arch. Eisenhuttenw., 14 (1940/41), p.307.
6) K. Endell and H. Hellbrugge: Natuwiss., 30 (1942), p.421.

7) J. O'M. Bockris, J. A. Kitchener, S. Ignatowitz and J. W. Tomlinson: Trans. Faraday Soc., 48 (1952), p.75.

8) J. O'M. Bockris, J. A. Kitchener and A. E. Davis: ibid, 48 (1952), p.536.

9) J. O'M. Bockris, and J. D. Mackenzie: Rev. Metall., 51 (1954), p.658.

10) J. O'M. Bockris and D. C. Lowe: Proc. Roy. Soc., A226 (1954), p.423.

11) J. O'M. Bockris, J. D. Mackensie and J. A. Kitchener: Trans. Faraday Soc., 51 (1955), p.1734.

12) J. O'M. Bockris and G. W. Mellors: J. Phys. Chem., 60 (1956), p.1321.

13) J. O'M. Bockris, J. W. Tomlinson and J. L. White: Trans. Faraday Soc., 52 (1956), p.299.

14) J. W. Tomlinson, M. S. R. Heines and J. O'M. Bockris: ibid, 54 (1958), p.1822.

15) M. G. Frohberg: Arch. Eisenhuttenw., 32 (1961), p.597.

16) P. Herasymenko and G. E. Speight: J. I. S. I., 166 (1950), p.169.

17) F. D. Richardson: Disc. Faraday Soc., (1948), p.244.

18) M. G. Frohberg and M. L. Kapoor: Stahl u Eisen, 91 (1971), p.182.

19) G. W. Toop and C. S. Samis: Trans. AIME, 224 (1962), p.878.

20) C. J. B. Fincham and F. D. Richardson: Proc. Roy Soc., A223 (1954), p.40.

21) C. R. Masson: ibid, A287 (1965), p201.

22) S. G. Whiteway, I. B. Smith and C. R. Masson: Can. J. Chem., 48 (1970), p.33.

23) P. J. Flory: J. Am. Chem. Soc., 74 (1952), p.2718.

24) P. J. Flory: "Principles of polymer chemistry" Cornell Univ. Press, Ithaca, N.Y., (1953).

25) C. R. Masson, I. B. Smith and S. G. Whiteway: Can. J. Chem., 48 (1970), p.201.

26) C. R. Masson, I. B. Smith and S. G. Whiteway: ibid. 48 (1970), p.1456.

27) M. L. Kapoor and M. G. Frohberg: Arch. Eisenhuttenw., 41 (1970), p.1035.

28) C. R. Masson: JISI, 210 (1972), p.89.

29) T. Yokokawa and K. Niwa: Trans. JIM, 10 (1969), p.3, 81.

30) E. D. Lacy: "The Vitreous State" (1955), The Glass Delegacy, University of Sheffield.

31) E. D. Lacy: Phys. Chem. Glasses, 4 (1963), p.234.

32) E. D. Lacy: ibid, 6 (1965), p. 171.

33) E. D. Lacy: Acta. Cryst., 18 (1965), p.141.

34) T. Emi, M. Shimoji: Japan Inst. Metals − (1967), (in Japanese) T. Emi: Doctor Thesis

35) W. R. Dickson and E. B. Dismukes: Trans. AIME., 224 (1962), p.505.

36) H. Kojima and C. R. Masson: Can. J. Chem., 47 (1969), p.4221.

37) J. H. Walsh, J. Chipman, T. B. King and N. J. Grant: J. Metals, 8 (1956), p. 1568.

38) M. Imai, H. Ooi and T. Emi: Tetsu to Hagane 50 (1962), p. 878. (in Japanese)

39) Y. Iguchi, S. Banya and T. Fuwa: Int'l Symp. on Met. Chem., (1971).

40) P. L. Sachder, A. Majdic and H. Schenck: Met. Trans., 3 (1972), p.1537.

41) J. Zarzycki: Disc. Faraday Soc., 32 (1961), p.38.

42) J. Zarzycki: "Non-crystalline Solids" John-Wiley, N.Y. (1960).

43) K. Furukawa: Disc. Faraday Soc., 32 (1961), p.53.

44) D. M. North and C. N. J. Wagner: J. Appl. Cryst., 2 (1969), p.149.

45) N. Iwamoto: Youyuen (Molten salts), 15 (1972), p.116. (in Japanese)

46) J. K. Wilmshurst: J. Chem. Phys., 39 (1963), p.2545.

47) J. P. De Luca and C. G. Bergeron: J. Am. Ceram. Soc., 54 (1971), p.191.

48) I. S. I. J., J. I. M. Kansai branch discussions (1.971, 11.13)

49) B. Harris and A. E. Jenkis: J. Sci, Instr., 36 (1959), p.238.

50) D. B. Caryll and R. G. Ward: JISI 207 (1967), p.28.

51) P. Predecki, A. W. Mullendore and N. J. Grant: Trans. AIME., 233 (1965), p.1581.

52) P. Duwez and R. H. Willens: Trans. AIME, 227 (1963), p.362.

53) L. Pargamin, C. H. P. Lupis and P. A. Flinn: Met. Trans., 3 (1972), p.2093.

54) C. W. Lents: Inorg. Chem., 3 (1964), p.574.

55) F. D. Richardson and L. E. Webb: Trans. Inst. Mining Met., 64 (1955), p.529.

56) C. R. Masson: JISI., 210 (1972), p.89.

57) J. Gotz, C. R. Masson and L. M. Castelliz: "Amorphous Materials" ed. by R. W. Douglas and B. Ellis, Wiley Interscience (1972), N.Y.

58) B. E. Warren and N. S. Ginglich: Phys. Rev., 46 (1934), p.368.

59) B. E. Warren, H. Krutter and D. Morningstar: J. Am. Ceram. Soc., 19 (1936), p.202.

60) B. E. Warren and J. Biscoe: J. Am. Ceram. Soc., 21 (1938), p.259.

61) R. L. Mozzi and B. E. Warren: J. Appl. Cryst., 3 (1970), p.251.

62) F. Zernicke and J. A. Prins: Zeit. Physik., 41 (1927), p.184.

63) W. H. Zachariasen: J. Am. Chem. Soc., 54 (1932), p.3841.

64) B. E. Warren and R. L. Mozzi: Acta. Cryst., 21 (1966), p.459.

65) R. Hoseman and K. Lemm and H. Drens: Zeit. Phys. Chem., 41 (1964), p.121.

66) C. N. J. Wagner "Liquid metals, chemistry and physics" ed. by S. Z. Beer, Marcel Dekker Inc. (1972), N.Y.

67) A. H. Silver and P. J. Bray: J. Chem. Phys., 29 (1958), p.984.

68) P. J. Bray, J. O. Edwards, J. C. O'Keefe, V. F. Ross and I. Tatsuzaki: ibid, 35 (1961), p.453.

69) P. J. Bray, M. Leventhal and H. O. Hooper: Phys. Chem. Glasses, 4 (1963), p.47.

70) M. Leventhal and P. J. Bray: ibid, 6 (1965), p.113.

71) R. F. Geller and E. N. Bunting: J. Res. nat. Bur. Stand., 18 (1937), p.585.

72) M. O. Samsoen: Ann. Phys., 9 (1928), p.35.

73) R. V. Adams and R. W. Douglas: 5th Int'l Congress on Glass, (1959).

74) N. Iwamoto: Trans. JWRI, 3 (1974), p.89.

75) N. Iwamoto: Welding, summer school text (1975), p.83 (in Japanese)

76) A. Adachi and N. Iwamoto: The 2nd Japan-USSR Joint Symp. on Phys. Chem. Met. Proc., (1969)

77) N. Iwamoto, Y. Makino, I. Satoh and K. Ogino: Technol. Repts. Osaka Univ., 22 (1972), p.113.

78) N. Iwamoto, Y. Makino and K. Ogino: Trans. JWRI., 1 (1972), p.17.

79) C. G. Dodd and G. L. Glen: J. Am. Ceram. Soc., 53 (1970), p.322.

80) R. G. Milkey: Am. Mineral., 45 (1960), p.990.

81) B. D. Saksena: Trans. Faraday Soc., 57 (1961), p.242.

82) I. Simon and H. O. McMahon: H. Chem. Phys., 21 (1953), p.23.

83) I. Simon and H. O. McMahon: J. Am. Ceram. Soc., 36 (1953), p.160.

84) F. Matossi and H. Bluschke: Z. Phys., 108 (1938), p.295.

85) P. E. Jellyman and J. P. Procter: Trans. Soc. Glass Tech., 39 (1955), p.173.

86) Y. Suginohara and T. Yanagase: Youyuen (Molten salts), 12 (1969), p.1, 151 (in Japanese)