Study on Slags of CaO- SiO_2 - Fe_2O_3 System by Mössbauer Spectroscopy[†]

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Abstract

The behaviours of Fe ions in the slags of CaO-SiO$_2$-Fe$_2$O$_3$ system were studied by Mössbauer spectroscopy. The results obtained suggest that especially ferric ions not only form some complex anions but also change the coordination state with the composition of the slag and partial oxygen pressure.

1. Introduction

In the structural study of molten slag, especially when transition elements are contained in slag, it must be noticed that coordination state of the transition metal ions will be changed by experimental circumstance, coexisting elements and so on. As it is very difficult to make researches on the molten state, generally many sorts of structural studies have been performed to the glassy specimen quenched and obtained from molten state. Mössbauer spectroscopy[1] was first applied to the glassy specimens of fused quartz and Pyrex glass by H. Pollack, M. DeCoster and W. Neuwirth[2]. Since then, Mössbauer spectroscopy has been applied to the study of the glasses containing Fe ions by many investigators,[3]~[10], it is now regarded to be useful techniques in order to know the structural behaviour of Fe ions in glasses.

Generally, it is said that ferrous ion in glass will take almost an octahedral site, and ferric ion will take a tetrahedral coordination in silicate glass but an octahedral in the case of phosphate glass[24]. However, octahedral coordinated ferric ion is also observed in some silicate glasses by Mössbauer spectroscopy. On the other hand, the state of ferrous ion in glass is also questionable because most of experiments were done in air and accordingly the quantity of ferrous ions was very small. Bishay and Kinawi observed experimentally band of tetrahedral ferrous ion by optical absorption measurement of the glasses produced under the strongly reduced atmosphere[11]. With the help of magnetic suceptibility study in silicate and borate glasses, Bishay reported that four-coordinated ferrous ion can be formed in glass.[12]. Goto and Ito also deduced that oxygen anions take a position around a ferrous cation in both tetra- and octahedral symmetries in glasses of the systems, Na_2O-SiO_2-Fe_2O_3 and Na_2O-P_2O_5-Fe_2O_3 from the optical absorption spectra[13].

In addition to the structural study, slag is to be recognized macroscopically from a view point of the reactivity. Considering the reactivity of the slag, how it acts as acid or base, that is to say, "basicity" is an important concept. Therefore, many effective indications for basicity have been given historically such as "excess base"[14] proposed on the basis of molecular theory of molten slag, "free oxygen mole number"[15] on the basis of ionic theory, and "B_L indication"[16] by Mori which is well accepted in welding.

The basic oxide is defined as the oxide which can supply O^{2-} ions, so the basicity of the slag should be defined as the easiness for the supply of O^{2-} ions, in the other words, from the activity of O^{2-} ion in slag. On the other hand, as pointed out by Guggenheim in the concentrated aqueous solution[17], the activity of individual ions in slag cannot in principle be determined

experimentally. Furthermore, Wagner indicated that the emf measurement of activity of O^{2-} ion in slag is impossible because of many assumptions[18]. Therefore Douglas, Nath and Paul deduced the activity of O^{2-} ion in slag with the data of redox equilibria[19]. Suginohara and Yanagase defined the basicity of the slag by using the redox data and the following equation:[20]

$$P^0 = \log [Fe^{2+}]/[Fe^{3+}]$$

where P^0 is basicity, $[Fe^{2+}]$ and $[Fe^{3+}]$ concentrations of Fe^{2+} and Fe^{3+} in the slag, respectively. Besides, Yokokawa, Tamura, Sato and Niwa determined the activity of O^{2-} ion in molten glass of the $Na_2O-P_2O_5$ system with the emf measurement and proposed the following equation by using the redox data[21]

$$\log ([Fe^{3+}]/[Fe^{2+}])^2 \frac{1}{P_{O_2}^{1/2}} = 0.32 \log (a_{O^{2-}}) + D$$

where P_{O_2} is partial oxygen pressure, $a_{O^{2-}}$ activity of O^{2-} ions, D constant.

In this paper, the authors aimed to study the behaviour of Fe ion in the $CaO-SiO_2-Fe_2O_3$ system by Mössbauer spectroscopy and from the redox reaction of Fe ion.

2. Experimental Procedures

The chemical compositions of samples are shown in Table 1. (Each sample contains 10 mole % Fe_2O_3.) As starting materials analytical-glade reagents were weighed correctly and mixed sufficiently. Each batch was held and equilibrated under a given atmosphere containing the partial oxygen pressure at 1600°C in a platinum crucible for about 8 hr. Gases used for controlling atmosphere were pure oxygen, air and CO-CO₂ mixed gas (1:1). The temperature of furnace was measured with 20Pt-40Rh thermocouple in an alumina tube. Each sample was quenched by raising out from the hot zone of the furnace. After

Table 1 Chemical Composition and equilibrating atomosphere

Sample	Mole %			P_{O_2} (atm)
	SiO_2	CaO_2	Fe_2O_3	
1	54	36		
2	45	45	10	1.0
3	36	54		
4	54	36		
5	45	45	10	0.21
6	36	54		
7	54	36		
8	45	45	10	10^{-6}
9	36	54		

cooling, the sample was crushed and fixed with a grease to perform Mössbauer study. The thickness of the specimen was regulated to obtain the maximum S/N Mössbauer spectrum.

Every component of Mössbauer equipment was constructed at Kobe University. The γ-ray source was a Co^{57}/Pd 0.5 mCi and moved in the constant velocity mode by an electro-mechanical transducer driving unit. The velocity was controlled exactly by a laser velocity meter. The absorption γ-ray was detected by scintillation counter and stored by multichannel analyzer up to larger than 2.5 x 10^5 counts. Every absorption spectra was analyzed with a computer program based on iterative least square procedure. The spectrum was given by the sum of Lorentzian shaped peaks.

$$F(I) = \sum_i H_i \left(\frac{1}{1+[2(X(I)-P_i)/W_i]^2} + \frac{1}{1+[2(X(I)-P_i-Q_i)/W_i]^2} \right)$$

where H_i is the height, P_i position, Q_i interval between two peaks, W_i half width.

3. Experimental Results

As an example, the typical spectra are shown in Figs. 1 and 2. The former is the spectra of glasses with various compositions produced in air. The latter is those of glasses with constant composition ($CaO/SiO_2=1/1$) produced under various oxygen partial pressures (P_{O_2}). The spectra consist of three peaks caused by Fe^{3+} and Fe^{2+} ions.

From Fig. 1, it will be seen that the left side peak shifts to higher velocity, on the contrary, the right one does not shift but increase in intensity as CaO/SiO_2 ratio decreases. This phenomenon is considered to be caused by the increase of Fe^{2+}/Fe^{3+} ratio according to the composition in glasses.

In Fig. 2, the intensity of the both outer side peaks increase and that of middle peak decreases, which accepts also the increase of Fe^{2+}/Fe^{3+} ratio with decrease of P_{O_2}.

Figures 3 and 4 show the ratio of Fe^{2+} to Fe^{3+} calculated from Mössbauer spectra by iterative least square procedure under the supposition that the spectra consist of two quadrapole splitting curves due to Fe^{3+} and Fe^{2+} ions. The calculation of $Fe^{2+}/(Fe^{2+} + Fe^{3+})$ was done with areas of splitting curves.

From Fig. 3, it will be anticipated that the fraction of $Fe^{2+}/(Fe^{2+} + Fe^{3+})$ decreases in any oxygen pressures as CaO mole % increases. From Fig. 4, it will be understood that the ratio decreases also in any compositions with the increasing of oxygen partial pressure.

In Tables 2 and 3 the isomer shift and quadrapole splitting of Fe^{2+} and Fe^{3+} ions are shown. The results of crystalline and vitreous materials obtained by several
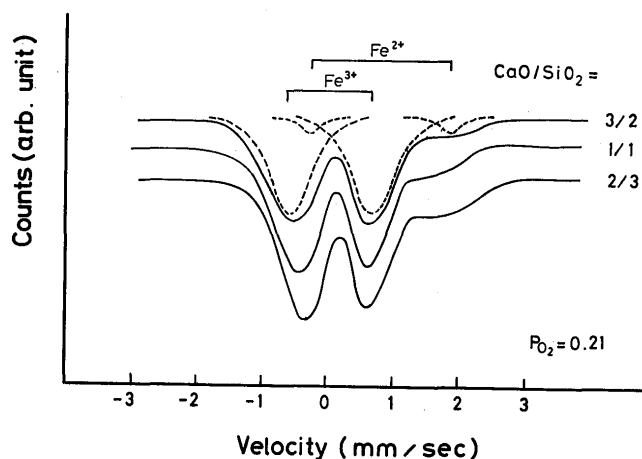
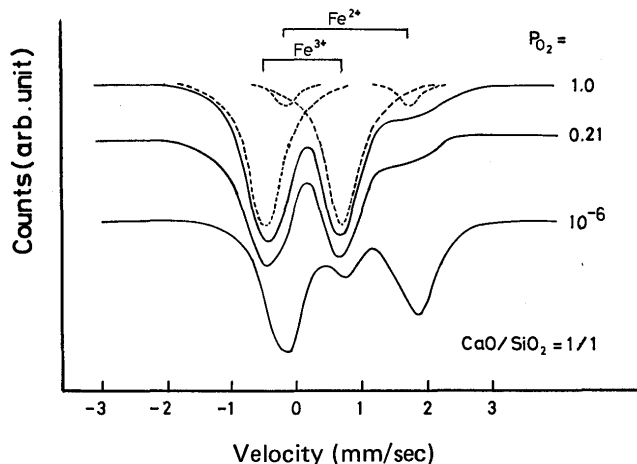Fig. 1 Mössbauer spectra of glasses with various compositions produced in air.

Fig. 2 Mössbauer spectra of glasses with constant composition $(CaO/SiO_2=1/1)$ produced under various oxygen pressures (P_{O_2}).
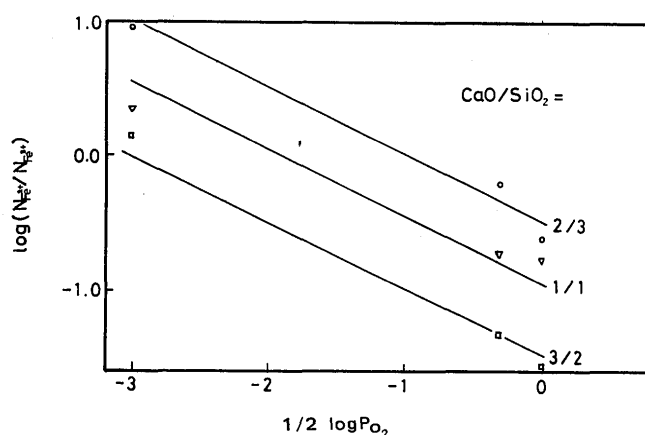

Fig. 3 Equilibrium dependence of $\log (N_{Fe^{2+}}/N_{Fe^{3+}})$ on $1/2 \log (P_{O_2})$ at various compositions.

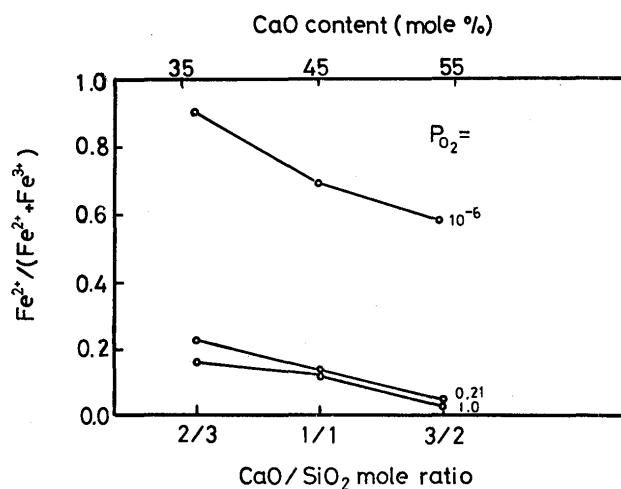Fig. 4 Equilibrium dependence of $Fe^{2+}/(Fe^{2+}+Fe^{3+})$ fraction on CaO/SiO_2 mole ratio at various oxygen pressures (P_{O_2}).

investigators are involved in the tables. The isomer shift gives the information about the electrondensity at nuclear site and it strongly depends on the Fe-O bond strength and the coordination number for oxygen. Isomer shift of Fe^{3+} ions in these glasses becomes smaller with the increase of CaO/SiO_2 ratio and as well as oxygen partial

Table 2. Dependence of isomer shift on composition and equilibrating oxygen pressure

Fe ion	CaO/SiO₂	P_{O_2} (atm)			crystal:
		1.0	0.21	10^{-6}	
Fe^{3+}	2/3	0.14	0.14	0.27	0.22 for Fe^{3+}_{oct}* 0.04 for Fe^{3+}_{tet}* glass:
	1/1	0.13	0.13	0.26	0.19 for Fe^{3+}_{oct}*
	3/2	0.10	0.10	0.17	0.02 for Fe^{3+}_{tet}*
Fe^{2+}	2/3	0.86	0.86	0.87	glass:
	1/1	0.91	0.84	0.82	0.87 for Fe^{2+}_{oct}**
	3/2	0.84	0.90	0.88	0.67 for Fe^{2+}_{tet}**

(mm/sec : Co/Pd) *ref. 5) **ref. 7)

Table 3. Dependence of quadrapole splitting on composition and equilibrating oxygen pressure

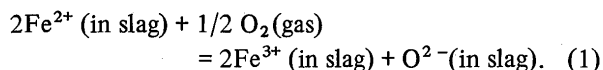| Fe ion	CaO/SiO₂	P_{O_2} (atm)			
		1.0	0.21	10^{-6}	
Fe^{3+}	2/3	1.22	1.19	0.97	glass:
	1/1	1.22	1.21	0.92	1.5 for Fe^{3+}_{tet}*
	3/2	1.27	1.25	1.15	0.8 for Fe^{3+}_{oct}*
Fe^{2+}	2/3	1.89	1.87	2.07	glass:
	1/1	1.73	1.82	2.12	2.0 for Fe^{2+}_{tet}**
	3/2	1.89	2.09	1.86	3.0 for Fe^{2+}_{oct}**

(mm/sec) *ref. 8) **ref. 7)

pressure. It must be considered that the phenomena would be caused by the formation of complex anions. On the other hand, for Fe^{2+} ion the isomer shift does not have clear dependence both on the composition and oxygen partial pressure. Our results for Fe^{2+} and Fe^{3+} ions agree with those obtained by other investigators in vitreous state[5,7]

The quadrapole splitting depends strongly on deviation from cubic symmetry of the local field. From the results obtained in this study, it seems that Fe^{2+} ion has a larger quadrapole splitting (Q.S.) than Fe^{3+} ion in any compositions and equilibrating atomosphers. It is considered that Q.S. value has no dependence on CaO/SiO ratios. On the other hand it does not change largely between P_{O_2} =0.21 and 1 atm but becomes smaller and larger at lowest oxygen pressure for Fe^{3+} and Fe^{2+} ions, respectively. This phenomenum may be explain by the coordination behaviours of Fe^{3+} and Fe^{2+} ions.

4. Discussions

It is necessary to assume some redox equations in considering the change of basicity depending on O^{2-} ions calculated from redox equilibrium. Bodsworth[22], Johnston[23] and Douglas[19] discussed redox reaction by using the following equation:

$$2Fe^{2+} \text{ (in slag)} + 1/2\ O_2(\text{gas})$$
$$= 2Fe^{3+} \text{ (in slag)} + O^{2-}(\text{in slag}). \quad (1)$$

The equilibrium constant for the reaction is as follows:

$$K = \frac{(a_{Fe^{3+}})^2\ a_{O^{2-}}}{(a_{Fe^{2+}})^2 (P_{O_2})^{1/2}} = \frac{(N_{Fe^{3+}})^2 (\gamma_{Fe^{3+}})^2\ a_{O^{2-}}}{(N_{Fe^{2+}})^2 (\gamma_{Fe^{2+}})^2 (P_{O_2})^{1/2}} \quad (2)$$

where a, γ and N mean the activity, activity coefficient and mole fraction of each ion, respectively. This relation shows that at any given temperature and partial oxygen pressure, the ratio of activities of a ferric and a ferrous ions (R.A.) varies inversely with the activity of an oxygen ion in the slag. According to Bodsworth[22], this phenomenon can be interpreted as follwos: Addition of the basic oxide to the slag makes a ferric ion to associate with an oxygen ion and therefore to form ferrite ion complex. This lowers the activity of a ferric ion. However, the bond energy between a ferrous ion and a ferrite ion complex is very much weaker than the energy between a ferrous ion and silicate anion. Hence a ferrous ion is replaced by a basic oxide, with the overall effect that the R.A. should be lowered to an increasing extent by addition of a basic oxide. To the contrary, it is evident from the present study that at given oxygen partial pressure the mole fraction ratio of ferric and ferrous ions increases with the addition of basic oxide, CaO, which

means qualitatively the increase of the activity of O^{2-} ion. If the equation (1) is adaptable in this case, this phenomenon can be interpreted with the result that the Fe^{3+}/Fe^{2+} activity coefficient ratio (R.γ.) is changed more rapidly than the corresponding activity ratio. This rapid change of R.γ. can be discussed with an isomer shift obtained from Mössbauer measurement. As is shown in Table 2, the value of isomer shift for ferric ion decreases with the addition of calcium oxide. It will perhaps means that the covalency of the bond between Fe^{3+} and O^{2-} ions increases and ferrite ion complex is stabilized further. It is, therefore, anticipated for $\gamma_{Fe^{3+}}$ to decrease. On the other hand, it seems that the isomer shift for ferrous ion has not remarkable dependence on the composition of the glass. Therefore, $\gamma_{Fe^{2+}}$ might be almost constant in the whole range of the composition. The total effect of the increasing of calcium oxide on the R.γ. is estimated to become smaller. However, the result is still open to question because of the propriety of equation (1).

It is considered that the increase of P_{O_2} equilibrated yields the increase of O^{2-} ion because the isomer shift depends on P_{O_2} in the same way as calcium oxide content. However, the production of O^{2-} ion in slag might contain two processes that are attributed to the redox reaction and the direct contribution of the atmospheric oxygen to parent melt of the slag. Hence it remains unclear whether the increase of P_{O_2} in the slag containing no redox ion has the same effect as the addition of basic oxide.

On the other hand, the ferric ion is considered to change from octahedral to tetrahedral site with increasing of both P_{O_2} and calcium oxide content from the comparison with the value of isomer shift in glass and in crystal. This will be interpreted as an amphoteric behaviour of ferric ion in slag. For a ferrous ion, however, no clear dependence can be found in isomer shift. The coordination state of a ferrous ion dosen't seem to have any change with the composition and seems to occupy an octahedral site in slag. (Even in the specimen treated in $P_{O_2}=10^{-6}$ atm, the change of the coordination site was not observed.) Accordingly, it is considered that a ferrous ion in lime silicate slag might not change the role as a modifier regardless of $a_{O^{2-}}$ change caused with the increasing of N_{CaO} and P_{O_2}.

Further studies are desired with the measurement of Mössbauer spectroscopy with much higher S/N ratio and other equipments such as an optical absorption means in order to investigate the basicity of slag on the basis of redox reaction.

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