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Citation	Transactions of JWRI. 3(1) P.53-P.57
Issue Date	1974-02
Text Version	publisher
URL	<a href="http://hdl.handle.net/11094/3624">http://hdl.handle.net/11094/3624</a>
DOI	
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# Behaviour of Transition Metal Ions in Slag (Report I)<sup>†</sup>

## —State of Titan Ion in CaO-SiO<sub>2</sub>-TiO<sub>2</sub> System—

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### Abstract

*Many sorts of conventional fluxes contain TiO<sub>2</sub> because it gives good properties for welding matters. The role of TiO<sub>2</sub> in flux remains unclear. It is important to study the state of titan ion for solving the behaviour of TiO<sub>2</sub> in slags. The state of titan ion in CaO-SiO<sub>2</sub>-TiO<sub>2</sub> system has been considered with the application of some spectroscopic means, that is to say, the measurements of infrared absorption, chemical shift of fluorescent X ray and X ray absorption. In these studies, it might be likely that Ti ion does not remain in complete octahedra coordination.*

### 1. Introduction

The weldability of flux depends on various physical properties such as viscosity, surface tension and so on. It has a great influence for getting a good shape of bead. Likewise, the reactivity of flux gives effect to the soundness of weld metal. Although there exists interrelation between the chemical and physical properties and the structure of flux, our knowledge is inadequate to develop new flux. In order to solve this problem, such a parameter as basicity has been considered to be available, but our intension is not always successful.

There are many sorts of fluxes containing TiO<sub>2</sub> in market because TiO<sub>2</sub> gives good properties for welding matters. However, the role of TiO<sub>2</sub> in flux remains unclear. As an example, the results of viscosity measurement of CaO-Al<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub> system are referred now. When substituting TiO<sub>2</sub> for Al<sub>2</sub>O<sub>3</sub> up to 9-10% in CaO-Al<sub>2</sub>O<sub>3</sub> system, the viscosity coefficient increases rapidly at 1500°C, but viscosity does not depend on TiO<sub>2</sub> content above 1550°C. On the other hand, when substituting TiO<sub>2</sub> for CaO, the viscosity coefficient increases over a wider range of experimental temperature. From these behaviour of TiO<sub>2</sub> in fluxes, it is impossible to interpret the similarity of titan ion to silicon ion.

Likewise, from the fact that the addition of SiO<sub>2</sub> or Al<sub>2</sub>O<sub>3</sub> to Na<sub>2</sub>O·2SiO<sub>2</sub> increases viscosity at 1400°C, TiO<sub>2</sub> decreases it reversely, it is recognized that the behaviour of titan ion is quite different from that of silicon ion.

Frohberg and Schenck have investigated in detail on the viscosity coefficient of CaO-SiO<sub>2</sub>-TiO<sub>2</sub> system

and SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub> system.<sup>1)</sup> The followings are their conclusions. It was noticed that SiO<sub>2</sub> content has great influence on the viscosity in SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub> system, but viscosity does not change noticeable in the case of low TiO<sub>2</sub> content. On the other hand, the isoviscosity lines are parallel to the variation of Al<sub>2</sub>O<sub>3</sub> content and the viscosity is independent to Al<sub>2</sub>O<sub>3</sub> in the case of CaO-Al<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub> system. CaO content gives additional effect to the influence of TiO<sub>2</sub>. They have summarized that TiO<sub>2</sub> generally decreases viscosity of the slag which contained CaO, SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub>.

Secondary, the results of electrical conductivity measurements will be briefly described. With increase of TiO<sub>2</sub> content in Na<sub>2</sub>O-SiO<sub>2</sub>-TiO<sub>2</sub> system, electrical conductivity decreases, but the value increases in CaO-SiO<sub>2</sub>-TiO<sub>2</sub> system. It seems as if Ti<sup>4+</sup> ion makes Ca<sup>2+</sup> ion to be free from the silicate network. However, in FeO-SiO<sub>2</sub> system, electric conductivity decreases with increasing of SiO<sub>2</sub>, but increases with the addition of TiO<sub>2</sub>.

From various results mentioned above, it was understood that it remain indistinct how Ti<sup>4+</sup> ion contributes to silicate network.

It has become practical to study solid slag because the investigation of slag structure in molten state is very difficult now. So, it has become important to obtain molten state of slag without change to room temperature.

According to random network theory of glass structure, it is essential for metal cations to occupy tetrahedral coordination in order to accommodate in network. This theory does not permit titan ions to be a networkformer because ionic radius of titan ion is

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suitable for octahedral coordination. Therefore, it is appropriate to consider  $\text{TiO}_2$  as a network modifier. Rao has investigated glassy specimens from alkali oxide- $\text{TiO}_2$  system and has concluded that  $\text{TiO}_2$  is a network former while being in octahedral coordination<sup>2)</sup>. He also studied specimens from  $\text{K}_2\text{O-SiO}_2\text{-TiO}_2$  system.<sup>3)</sup> He says that  $\text{TiO}_2$  reinforces the network from occupying tetrahedral coordination in the case of high silica content, but it weakens the network from occupying octahedral coordination in the case of low silica. He concluded that  $\text{TiO}_2$  has tendency to work as network former essentially.

The authors have intended for studying the state of titan ion, that is to say, to know coordination number, and the state of Ti-O bond. These knowledge play an important role for solving the behaviour of  $\text{TiO}_2$  in slags. In this report, the state of titan ion in slags has been considered with the application of some spectroscopic means.

## 2. Experimental procedures

The chemical compositions of each slags are given in **Table 1** and shown in **Fig. 1**. Every components of analytical grade reagents were correctly weighed and mixed sufficiently. Specimens near one gram were supplied to one experiment. After held for 2 hours at the temperature of  $100^\circ\text{C}$  above melting point, it was dropped into mercury ice-cooled.

Infra-red absorption measurements were performed with 225-type spectrometer (Hitach Co. Ltd.). Every specimens were mixed with nujole. Fluorescent X-ray studies were carried on with X-ray spectrometer system (Rigaku Denki Co. Ltd.). Chromium and tungsten targets and  $\text{LiF}$  (200) and (220) as dispersion crystal were used. X-ray absorption measurements were done with GF-3 (Rigaku Denki Co. Ltd.) and 400 multi channel analyzer (Tullamore Model PIP 400).

Table 1. Chemical composition of specimens.

Slag No.	Mole %		
	$\text{TiO}_2$	$\text{SiO}_2$	$\text{CaO}$
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
6	7.5	47.2	45.3
7	7.5	39.6	53.0
8	56.1	56.1	36.5

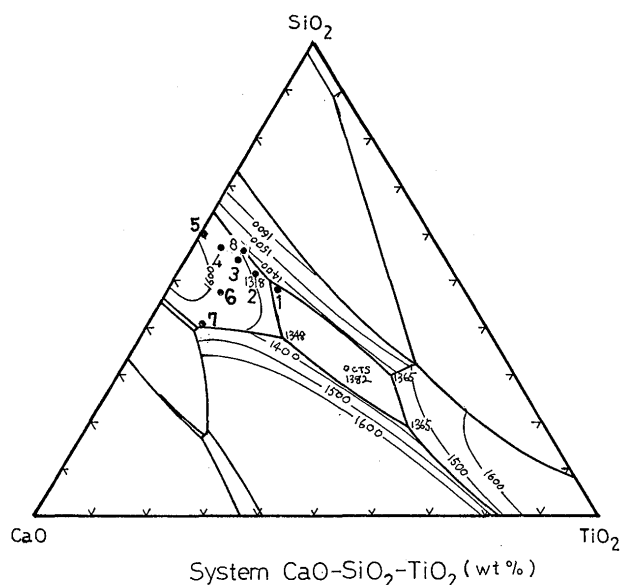


Fig. 1. Specimens studied in the system  $\text{SiO}_2\text{-CaO-TiO}_2$ .

## 3. Experimental results

As an example, typical result by X-ray diffraction patterns of slag rapidly quenched is shown in **Fig. 2**. It will be seen that the patterns obtained are broad and there is no proof of crystallized matters. It was certified that every specimens did not show crystallization similar to this result.

In **Fig. 3**, the variation of infra-red absorption results with varying  $\text{TiO}_2$  composition from 0 to 15.5 mole% of the specimens which have constant ratio of  $\text{CaO/SiO}_2 = 0.71$  are shown.

Likewise, the variation of infra-red absorption results with changing  $\text{CaO/SiO}_2$  ratio from 0.65 to 1.3 of the specimens having constant  $\text{TiO}_2$  content are shown in **Fig. 4**. It is known that the broad absorption band ranging from  $1200$  to  $900\text{ cm}^{-1}$  is caused by the stretching vibration ( $\nu_3$ ) of Si-O bond, and the absorption band appeared at about  $500\text{ cm}^{-1}$  is caused by the bending vibration ( $\nu_4$ ) of Si-O bond. The absorption band appeared at about  $720\text{ cm}^{-1}$  is caused to nujole.

As an example, the comparison of chemical shift of  $\text{TiK}_\beta$  of between titan metal and slag containing  $\text{TiO}_2$  are shown in **Fig. 5**. As an example, the comparison of X-ray absorption spectrum between same samples are shown.

## 4. Discussion

In Figs. 3 and 4, two absorption bands were determined. The higher frequency absorption band is due to the stretching vibration ( $\nu_3$ ) of Si-O bond and that of lower frequency ( $\nu_4$ ) is caused by bending of

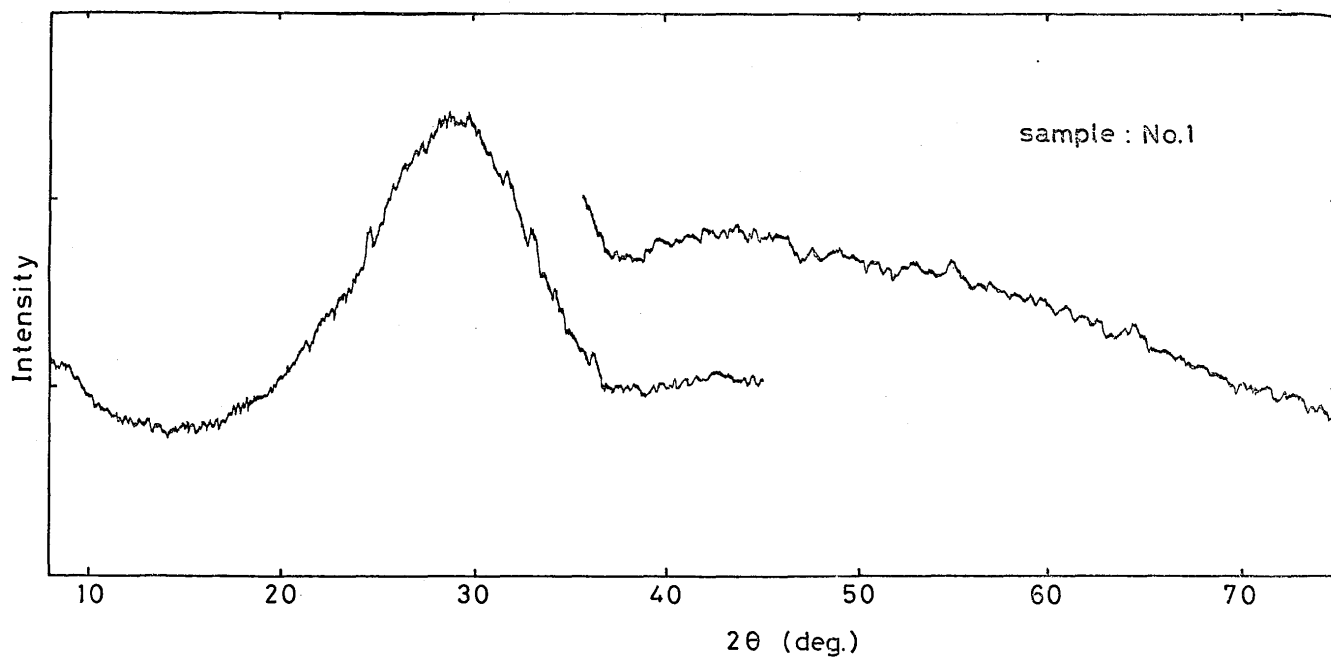
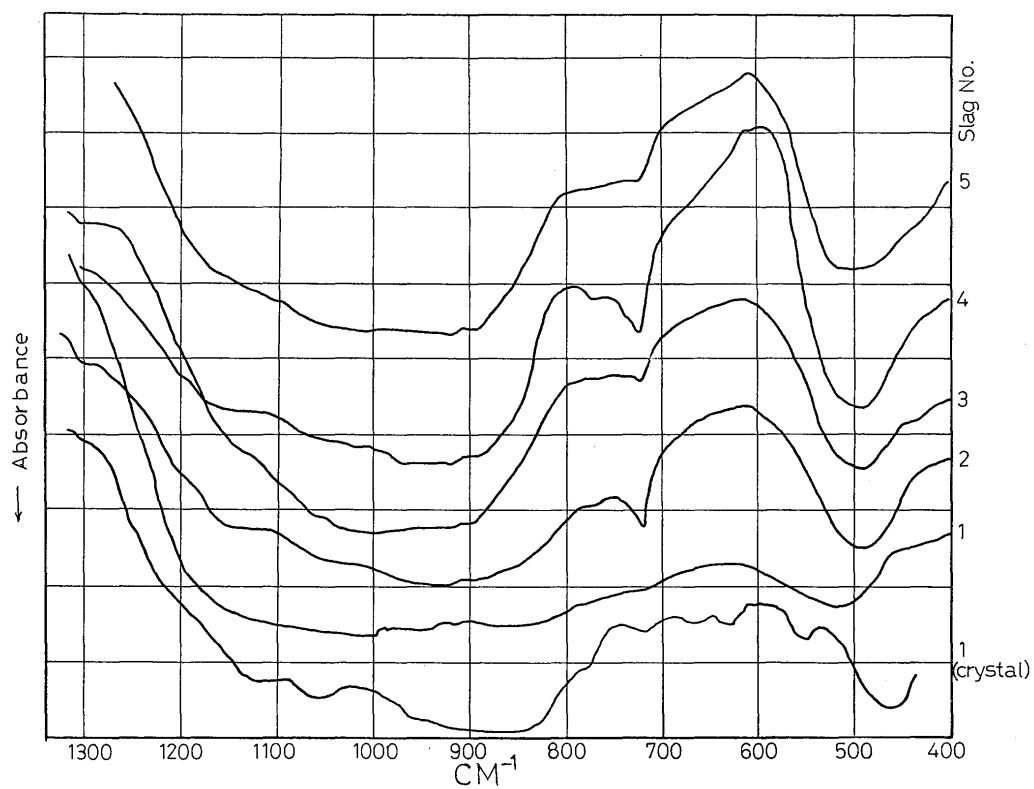


Fig. 2. X-ray diffraction pattern: sample No. 1.

Fig. 3. Infrared spectra of the slags in the case of  $\text{CaO}/\text{SiO}_2=0.71$ .

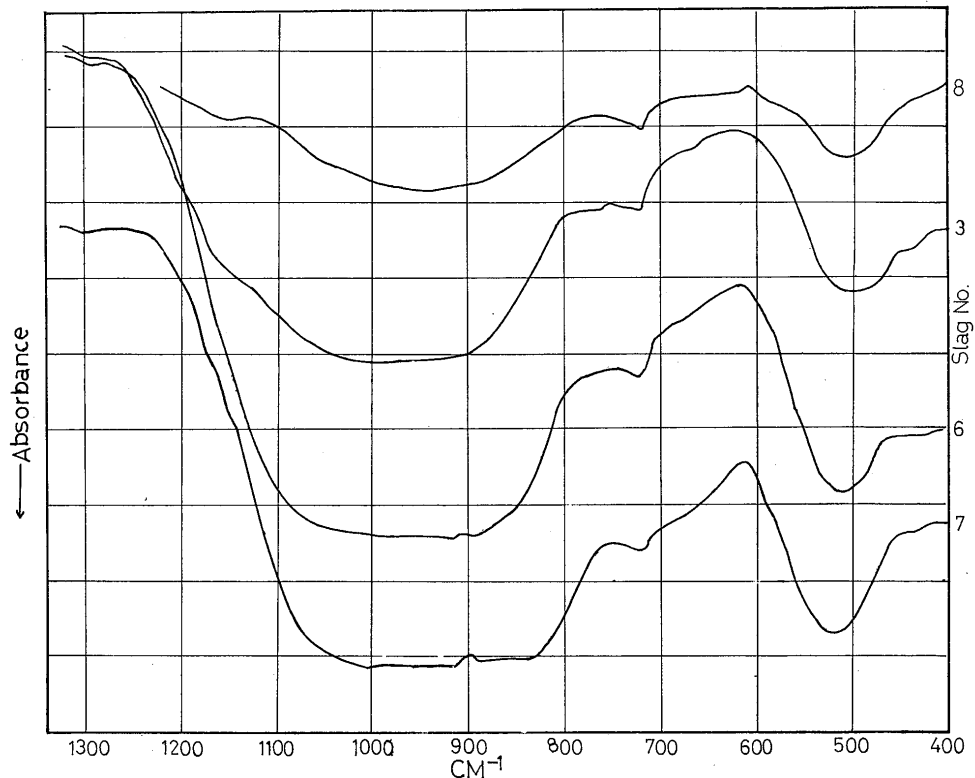


Fig. 4. Infrared spectra of the slags in the case of constant  $\text{TiO}_2$  content.

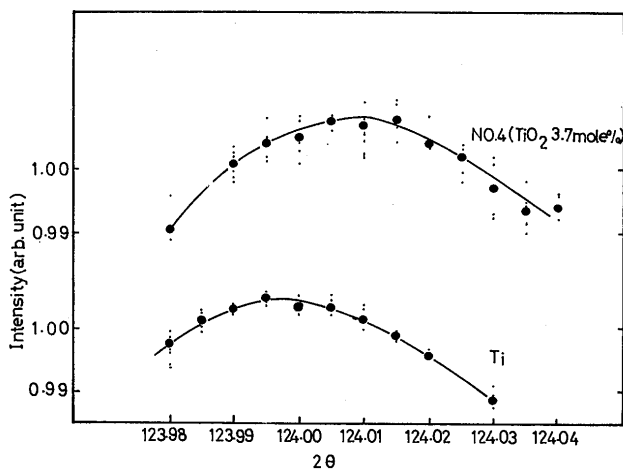


Fig. 5. Fluorescent X-ray spectra of Ti in Ti metal and sample No. 4.

Si-O bond as is generally known. Respectively,  $\nu_3$  and  $\nu_4$  bands shift to lower and higher frequency with the increase of CaO content. The variation is understood from the knowledge that CaO behaves as modifier in slag. These experimental results agree well with the results of Suginozawa et al.<sup>4)</sup>

With the increase of  $\text{TiO}_2$  content, every specimens except No. 1 have shown the same results that  $\nu_3$  band shifts to lower frequency in contrary to the fixation of  $\nu_4$  band. On the other hand, No. 1 slag containing 15.5 mole % has shown  $\nu_4$  band shift to

higher frequency than those in the specimens containing lower  $\text{TiO}_2$  content. However, the cause of the shift is unclear at this point.

Furthermore, there exists the difficulty to obtain glassy materials in the samples having constant  $\text{CaO}/\text{SiO}_2=0.71$  ratio when they contained  $\text{TiO}_2$  content above 30 wt %. From the absorption profiles, it is anticipated that a certain change occurs in the structure of slag. The cause of the difference of the absorption results between specimen (No. 1) and another samples correspond to the inequality of the crystallization. In Fig. 3, the absorption spectrum of crystallized specimen (No. 1) is also shown for comparison. The spectrum contains the occurrences of fine structures and the  $\nu_4$  band has largely different frequency when compared with glassy specimen. It is apparent that the vanishing of the fine structures in the glassy state means the variation to random arrangement of structural groups. According to Dachille and Roy<sup>5)</sup>, and Tarte<sup>6)</sup>, it was indicated that the main infra-red absorption bands which corresponds to the stretching modes of metal ion-O shift to higher frequency if metal ion has a lower coordination number. In the case of Ti-O, the absorption band appears in the frequency range from 500 to 650  $\text{cm}^{-1}$  when titan ion has a octahedral coordination. Whereas, the absorption band shifts to 690~850  $\text{cm}^{-1}$  when titan ion has tetrahedral coordination. In this

study, absorption bands are not found because of the scanty of  $\text{TiO}_2$  content and  $\text{SiO}_2$  absorption bands. Furthermore, Raman spectrum was obtained because of obtaining Ti-O spectrum without hindrance of another vibration modes. As a result of the present time, Raman experiment was unsuccessful because of the appearance of the strong emission uncleared from which the cause was induced.

From the comparison of Figs. 3 and 4, it is understood that  $\text{TiO}_2$  might take same role as  $\text{CaO}$  in slag.

If the coordination of titan or the state of Ti-O bond is varied, the energy level of valence electron of titan changes. This consideration suggests that the wavelength of characteristic X-ray of titan will vary. Dodd and Glen<sup>7)</sup> observed the chemical shift of  $\text{SiK}_\beta$  in glasses shift to higher energy due to the destabilization of Si-O bond.

An example of the measurements of  $\text{TiK}_\beta$  is shown in Fig. 5.  $\text{K}_\beta$  line of Ti in slag shifts to lower energy when compared with the results from metallic titan. Another specimens have shown the similar tendency. These results are explained by molecular orbital theory that the energy of the valence electron of titan becomes lower because titan combines with oxygen. At this stage there remains uncertainly to discuss about detailed points because the resolution angle of fluorescent X-ray instrument is  $0.01^\circ$  in  $2\theta$ . It is difficult to discuss the variation of energy state in the vicinity of  $\text{Ti}^{4+}$  ion with this means.

In Fig. 6, the absorption spectra of titan in the sample (No. 1) and standard  $\text{TiO}_2$  are shown. The difference of titan spectrum is remarkable. The variation at the higher energy region beyond absorption

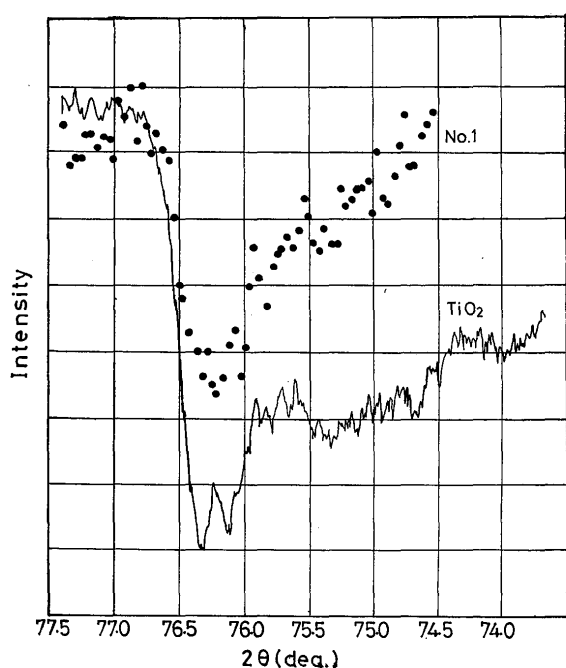


Fig. 6. X-ray absorption spectra of Ti in  $\text{TiO}_2$  and sample No. 1.

edge corresponds generally to the change of the coordination. The coordination of titan in slag might be different from perfect octahedra coordination. It is expected that X-ray absorption means will give much information about the variation of circumstance in the vicinity of  $\text{Ti}^{4+}$  in slags.

## 5. Conclusion

Measurements of infrared absorption, chemical shift of fluorescent X-ray, and X-ray absorption were carried out about glassy samples of the  $\text{SiO}_2$ - $\text{CaO}$ - $\text{TiO}_2$  system. Middle-infrared absorption measurement gave only informations of  $\nu_3$  and  $\nu_4$  vibration of Si-O bond. It was not clear in this wavelength range (middle-infrared) what state  $\text{Ti}^{4+}$  ions exist in. In fluorescent X-ray measurement, it was observed that the  $\text{K}_\beta$  line of Ti in slag shifts slightly toward low energy level in comparison with Ti metal. However, the accuracy was so insufficient that the state of  $\text{Ti}^{4+}$  ion in slag could not be discussed with the results. X-ray absorption measurement appeared apparent difference between the profile of absorption spectra of Ti in slag and that of Ti in  $\text{TiO}_2$ . The authors have considered that X-ray absorption measurement may be the good method for studying the state of  $\text{Ti}^{4+}$  ion in slag.

In our investigation, it could not be concluded whether  $\text{TiO}_2$  is a slag network former or a modifier in the composition range studied. It might be likely that Ti ion does not remain in complete octahedra coordination.

## Acknowledgement

Authors thank to facilities for X-ray absorption research to Prof. Tsutsumi in Osaka Prefectural University and for fluorescent X-ray research to Rigaku Denki Co. Ltd.

## References

- 1) H. Shenck und M. G. Froberg: *Arch. Eisenhüttenw.*, 33 (1962) S. 421.
- 2) Bh. V. Rao: *J. Am. Ceram. Soc.*, 147 (1964) p. 455.
- 3) Bh. V. Rao: *Phys. Chem. Glasses*, 4 (1963) p. 22.
- 4) Y. Sugihara and T. Yanagase: JIM symposium at 25th Nov. in 1972.
- 5) F. Dacheille and R. Roy: *Z. Krist.*, 111 (1959) p. 462.
- 6) P. Tarte: "Physics of Non-Crystalline Solids" Edited by J. A. Prins. Interscience Publishers, Div. of John Wiley and Sons, Inc., New York, 1965.
- 7) C. G. Dodd and G. L. Glen: *J. Am. Ceram. Soc.*, 53 (1970) p. 322.