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Behaviour of Transition Metal Ions in Slag (Report I)[†]

—State of Titan Ion in CaO-SiO₂-TiO₂ System—

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Abstract

Many sorts of conventional fluxes contain TiO₂ because it gives good properties for welding matters. The role of TiO₂ in flux remains unclear. It is important to study the state of titan ion for solving the behaviour of TiO₂ in slags. The state of titan ion in CaO-SiO₂-TiO₂ 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 TiO₂ in market because TiO₂ gives good properties for welding matters. However, the role of TiO₂ in flux remains unclear. As an example, the results of viscosity measurement of CaO-Al₂O₃-TiO₂ system are referred now. When substituting TiO₂ for Al₂O₃ up to 9-10% in CaO-Al₂O₃ system, the viscosity coefficient increases rapidly at 1500°C, but viscosity does not depend on TiO₂ content above 1550°C. On the other hand, when substituting TiO₂ for CaO, the viscosity coefficient increases over a wider range of experimental temperature. From these behaviour of TiO₂ in fluxes, it is impossible to interpret the similarity of titan ion to silicon ion.

Likewise, from the fact that the addition of SiO₂ or Al₂O₃ to Na₂O·2SiO₂ increases viscosity at 1400°C, TiO₂ 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-SiO₂-TiO₂ system

and SiO₂-Al₂O₃-TiO₂ system.¹⁾ The followings are their conclusions. It was noticed that SiO₂ content has great influence on the viscosity in SiO₂-Al₂O₃-TiO₂ system, but viscosity does not change noticeably in the case of low TiO₂ content. On the other hand, the isoviscosity lines are parallel to the variation of Al₂O₃ content and the viscosity is independent to Al₂O₃ in the case of CaO-Al₂O₃-TiO₂ system. CaO content gives additional effect to the influence of TiO₂. They have summarized that TiO₂ generally decreases viscosity of the slag which contained CaO, SiO₂ and Al₂O₃.

Secondary, the results of electrical conductivity measurements will be briefly described. With increase of TiO₂ content in Na₂O-SiO₂-TiO₂ system, electrical conductivity decreases, but the value increases in CaO-SiO₂-TiO₂ system. It seems as if Ti⁴⁺ ion makes Ca²⁺ ion to be free from the silicate network. However, in FeO-SiO₂ system, electric conductivity decreases with increasing of SiO₂, but increases with the addition of TiO₂.

From various results mentioned above, it was understood that it remains indistinct how Ti⁴⁺ 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 TiO_2 as a network modifier. Rao has investigated glassy specimens from alkali oxide- TiO_2 system and has concluded that TiO_2 is a network former while being in octahedral coordination²⁾. He also studied specimens from $\text{K}_2\text{O}-\text{SiO}_2-\text{TiO}_2$ system.³⁾ He says that 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 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 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°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 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 %		
	TiO_2	SiO_2	CaO
1	15.5	49.3	35.2
2	11.4	51.7	36.9
3	7.5	54.0	38.5
4	3.7	56.2	40.1
5	0	58.3	41.7
6	7.5	47.2	45.3
7	7.5	39.6	53.0
8	56.1	56.1	36.5

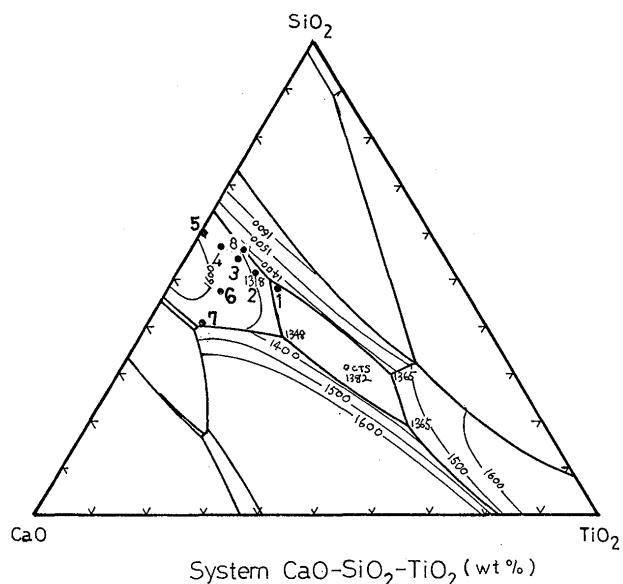


Fig. 1. Specimens studied in the system $\text{SiO}_2-\text{CaO}-\text{TiO}_2$.

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 TiO_2 composition from 0 to 15.5 mole% of the specimens which have constant ratio of $\text{CaO}/\text{SiO}_2 = 0.71$ are shown.

Likewise, the variation of infra-red absorption results with changing CaO/SiO_2 ratio from 0.65 to 1.3 of the specimens having constant TiO_2 content are shown in **Fig. 4**. It is known that the broad absorption band ranging from 1200 to 900 cm^{-1} is caused by the stretching vibration (ν_3) of Si-O bond, and the absorption band appeared at about 500 cm^{-1} is caused by the bending vibration (ν_4) of Si-O bond. The absorption band appeared at about 720 cm^{-1} is caused to nujole.

As an example, the comparison of chemical shift of TiK_β of between titan metal and slag containing 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 (ν_3) of Si-O bond and that of lower frequency (ν_4) is caused by bending of

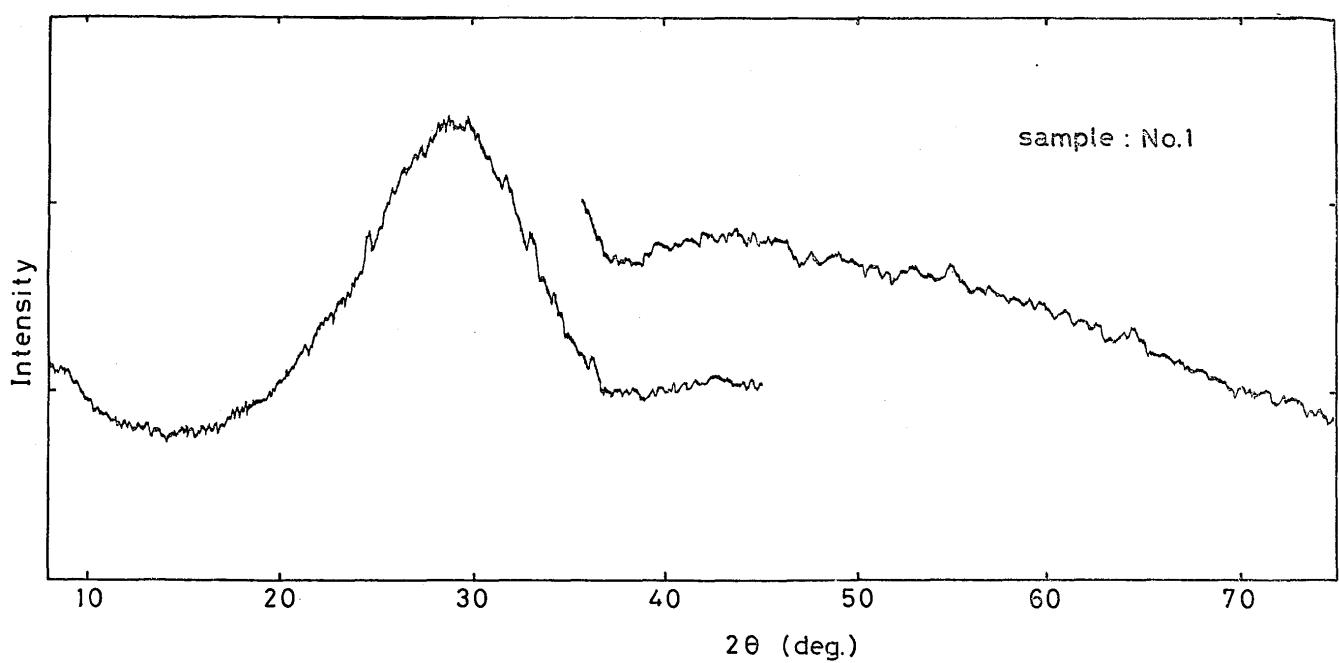


Fig. 2. X-ray diffraction pattern: sample No. 1.

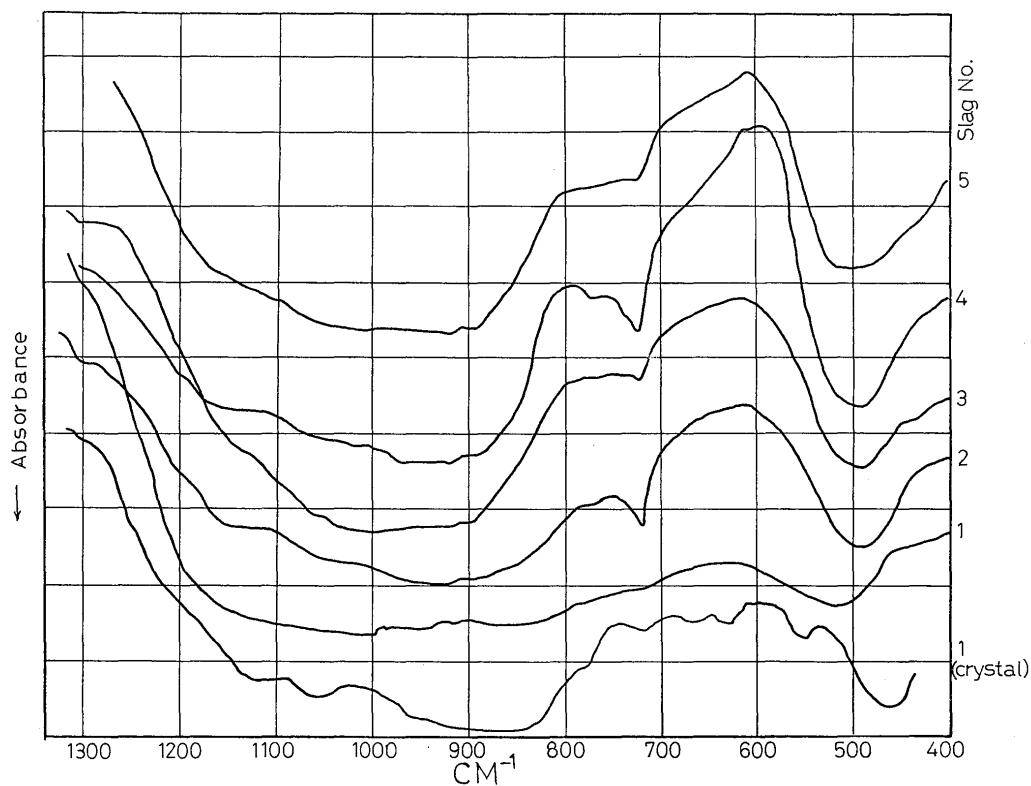


Fig. 3. Infrared spectra of the slags in the case of $\text{CaO}/\text{SiO}_2 = 0.71$.

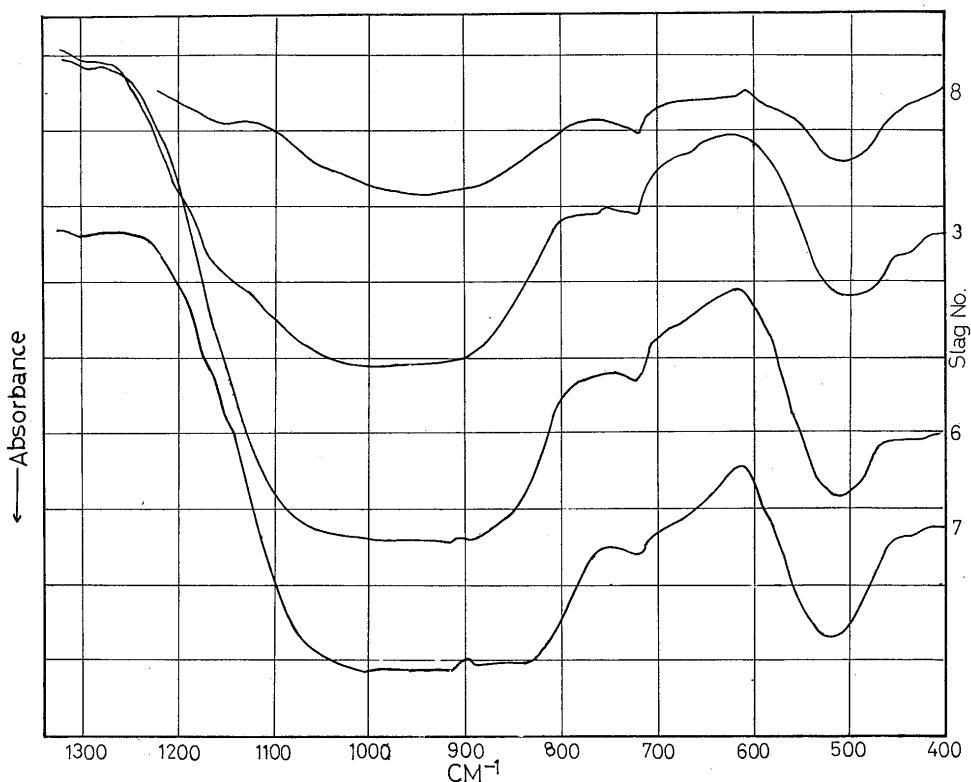
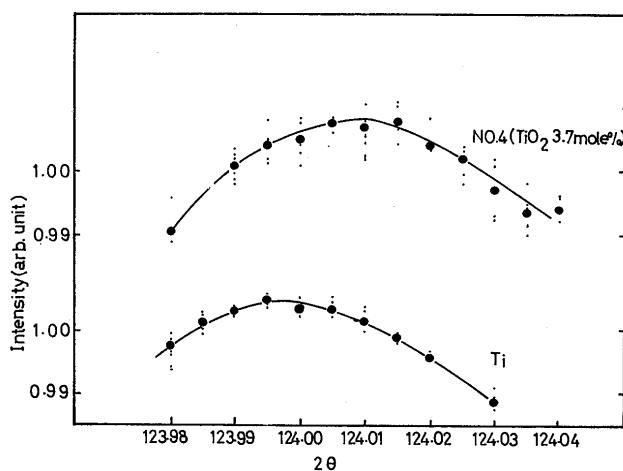
Fig. 4. Infrared spectra of the slags in the case of constant TiO_2 content.

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

Si-O bond as is generally known. Respectively, ν_3 and ν_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 Sugino et alii⁴.

With the increase of TiO_2 content, every specimens except No. 1 have shown the same results that ν_3 band shifts to lower frequency in contrary to the fixation of ν_4 band. On the other hand, No. 1 slag containing 15.5 mole % has shown ν_4 band shift to

higher frequency than those in the specimens containing lower 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 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 ν_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 Roy⁵, and Tarte⁶, 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 cm^{-1} when titan ion has a octahedral coordination. Whereas, the absorption band shifts to 690~850 cm^{-1} when titan ion has tetrahedral coordination. In this

study, absorption bands are not found because of the scanty of TiO_2 content and 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 TiO_2 might take same role as 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 Glen⁷ observed the chemical shift of SiK_{β} in glasses shift to higher energy due to the destabilization of $Si-O$ bond.

An example of the measurements of SiK_{β} is shown in **Fig. 5**. K_{β} 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° in 2θ . It is difficult to discuss the variation of energy state in the vicinity of Ti^{4+} ion with this means.

In **Fig. 6**, the absorption spectra of titan in the sample (No. 1) and standard TiO_2 are shown. The difference of titan spectrum is remarkable. The variation at the higher energy region beyond absorption

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 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 $SiO_2-CaO-TiO_2$ system. Middle-infrared absorption measurement gave only informations of ν_3 and ν_4 vibration of $Si-O$ bond. It was not clear in this wavelength range (middle-infrared) what state Ti^{4+} ions exist in. In fluorescent X-ray measurement, it was observed that the K_{β} 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 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 TiO_2 . The authors have considered that X-ray absorption measurement may be the good method for studying the state of Ti^{4+} ion in slag.

In our investigation, it could not be concluded whether 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

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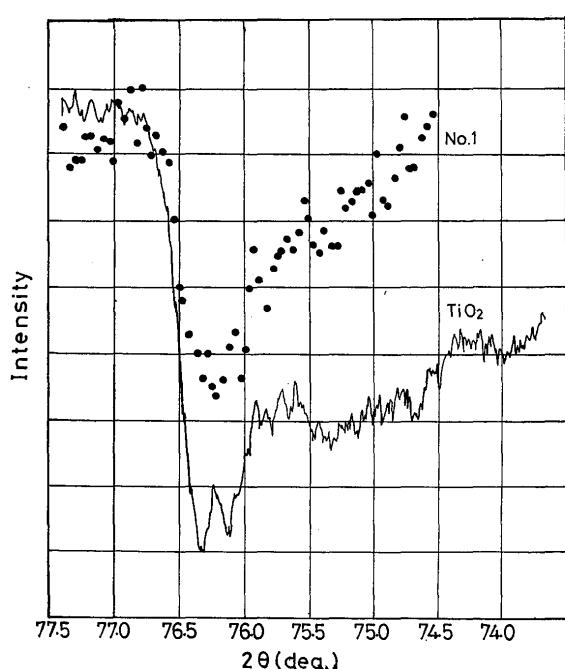


Fig. 6. X-ray absorption spectra of Ti in TiO_2 and sample No. 1.