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Structural Investigation on Ti^{3+} Ion in Soda-silicate Slag†

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Abstract

State of titanium ion in soda silicate slags was investigated by optical absorption and electron spin resonance (ESR) spectroscopies in order to clarify the effect of titanium ion in slag on the properties of weld metal and spilling property of slag in welding process. An optical absorption with a shoulder was observed at about $20,000\text{ cm}^{-1}$ in the slags produced under the reducing condition ($P_{O_2}=2.1 \times 10^{-9}\text{ atm.}$). ESR absorption was also observed near $g=1.924$ in these slags. These absorptions were assigned to Ti^{3+} ions in an octahedral environment with tetragonal distortion. The observations of another optical absorption near $8,300\text{ cm}^{-1}$ and appearance of a shoulder near $g=1.985$ suggested that there exists Ti^{3+} ions in an octahedral environment with trigonal distortion in high silica content. Based on the structural consideration of silicate slag, it is indicated that tetragonally and trigonally distorted environments arise from the octahedrally coordination of free and non-bridged oxygens to Ti^{3+} ions, that is, $Ti^{3+} O_{6-n}^- O_n^{2-}$ units, and the former environment is due to $Ti^{3+} O_4^- O_2^{2-}$ and $Ti^{3+} O_5^- O^{2-}$ units.

KEY WORDS: (Ti^{3+} ion) (State analysis) (Slag) (ESR) (Optical absorption)

1. Introduction

Fluxes containing titania are widely used in various welding processes. Titania is added to the flux in order to improve various properties of weld metal and weldability, so that it is important to elucidate the behaviors of Ti ions in welding processes.

Behaviors of Ti ions in metallurgical slags have been investigated by several workers¹⁻⁴⁾ in physical properties or structurally. It has been considered that titania acts as an amphoteric component⁵⁾ in slags, that is, behaves as network-former or modifier depending on the composition of slag. Although the coordination of Ti^{4+} ions has been investigated by various methods^{6,7)} such as the neutron diffraction, the details on structural information of Ti^{4+} ion remain unclear.

In the system of atmosphere-slag-molten metal, it is expected that oxygen potential of slag is low near molten metal whereas it is high near surface of slag. Therefore, Ti ions in the slag near molten metal prefer to be in a lower valency states (Ti^{3+} or Ti^{2+}) than Ti^{4+} . Generally, it is easily expected that titanium can be in the form of Ti^{2+} or Ti^{3+} ion under reducing conditions. The spectrum of Ti^{3+} ions can be observed by optical absorption or electron spin resonance (ESR) because they have lonepair $3d^1$ electron. Some investigators⁸⁻¹⁰⁾ reported by optical absorption or ESR that Ti ions are partially in the form of Ti^{3+} -state in glasses produced

under reducing conditions. They considered that most of Ti^{3+} ions are in an octahedral site in the glasses. The coordination number of Ti^{3+} ions in slags is important in the structure theory of slag, too. We think more detail states of Ti^{3+} ions must be known in order to elucidate the slag-metal reaction.

In this study, in order to elucidate the state of Ti^{3+} ions in slags under reducing conditions, the structural investigation of Ti^{3+} ions is enforced by using optical absorption and ESR methods.

2. Experimentals

Specimen slags were prepared from analytical reagent Na_2CO_3 , SiO_2 and TiO_2 . After the reagents were accurately weighed, they were mixed sufficiently using acetone as the immersion liquid and then were well dried. Mixtures were preliminarily melted in platinum crucibles at 1600°C in air using an electric furnace, then were cooled in air. Then, they were remelted and held for 3 hours at 1600°C under reducing conditions and they were cooled in the top of the furnace. Heating temperature was controlled at $1600 \pm 2^\circ\text{C}$ using PID. CO and CO_2 gases were mixed using the gas-mixer and this mixed gas was blown into the furnace. The samples for optical measurements were ground and polished in the form of discs with different thickness while the samples for ESR measurements were pulverized in an agate mortar and pestle.

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Optical absorption spectra were measured with absorbance mode by a spectrometer of Hitachi 323 type. The thickness of specimens was measured with a micrometer and the optical density was calculated from the absorbance by Lambert-Beer's equation.¹¹⁾ ESR spectra were measured by a spectrometer of Varian E-109 type with X-band at room temperature. Powder specimens were weighed accurately and then sealed in evacuated silica tubes. These specimens were introduced in the cavity resonator with the help of silica glass tubes.

3. Results

Optical absorption spectra of $10\text{Na}_2\text{O}-85\text{SiO}_2-5\text{TiO}_2$ slags produced under various oxygen pressures are shown in Fig. 1. A strong absorption (Peak 1) and a shoulder are observed near $20,000\text{ cm}^{-1}$ and $15,000\text{ cm}^{-1}$ respectively. With lowering the oxygen pressure another absorption (Peak 2) appears near $8,300\text{ cm}^{-1}$.

Figure 2 shows optical absorption spectra of the slags which were produced under the reducing condition that P_{O_2} is 2.1×10^{-9} atm. as a function of SiO_2 content. These slags contain 5 mol% TiO_2 . Figure 3 shows optical absorption spectra of Ti^{3+} ions in the slags as a function of TiO_2 content produced under the same reducing condition. As SiO_2 content or TiO_2 content increases, the optical density increases.

The electron spin resonance spectra of the slags containing 5 mol% TiO_2 produced under the partial

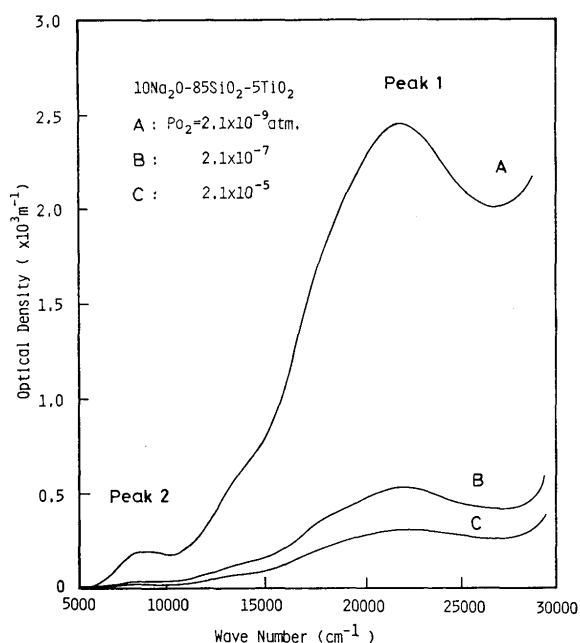


Fig. 1 The optical absorption spectra of soda silicate slags containing 5.0 mol% TiO_2 produced under various reducing conditions

oxygen pressure of 2.1×10^{-9} atm. are shown in Fig. 4. An resonance is observed near 3,530 gauss ($g=1.924$) and a shoulder is observed near 3,430 gauss ($g=1.985$) in the slags containing much of SiO_2 . Table 1 shows values of the g -factor and the intensity of the resonance near 3,530 gauss.

Figure 5 shows the intensity of resonance near

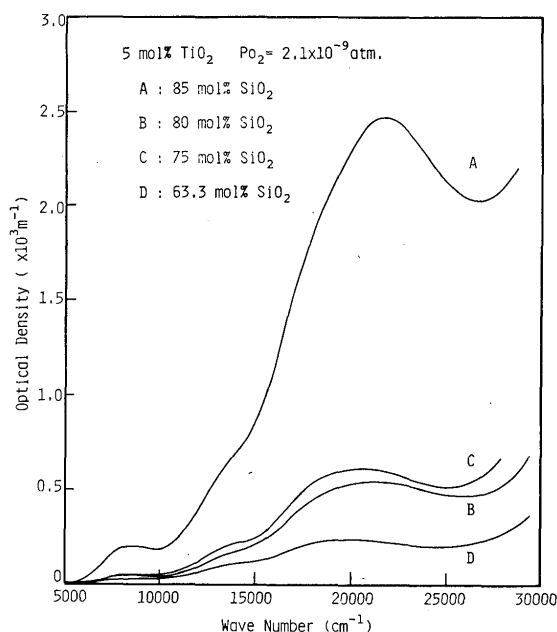


Fig. 2 The optical absorption spectra of soda silicate slags containing 5.0 mol% TiO_2 produced under the reducing condition ($P_{\text{O}_2}=2.1 \times 10^{-9}$ atm., 1600°C)

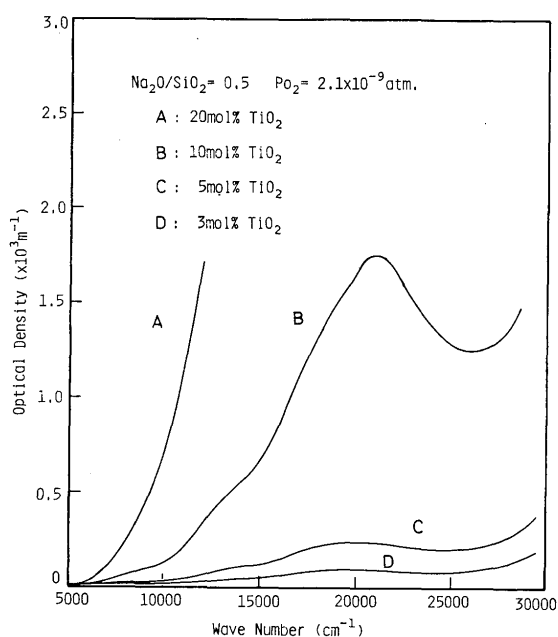
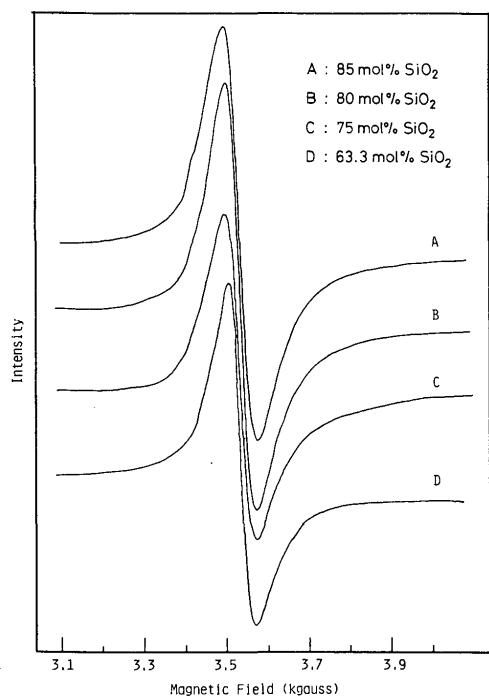
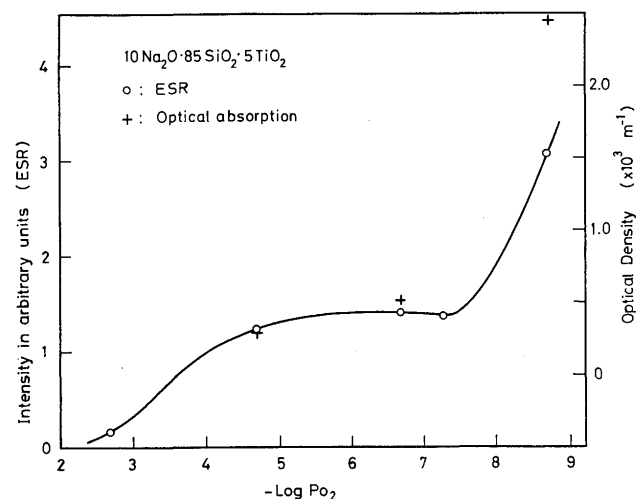
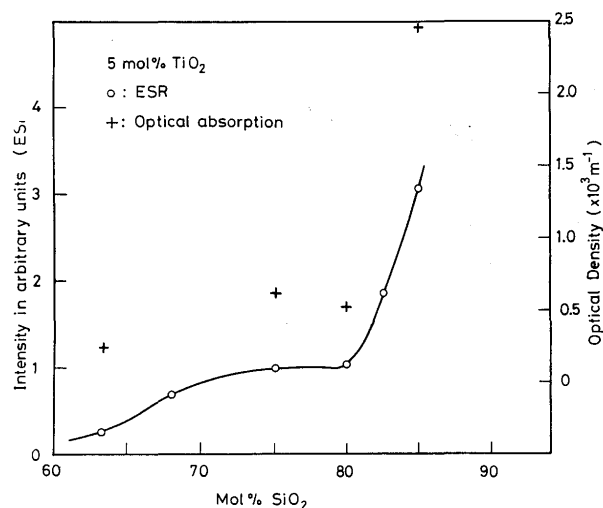


Fig. 3 The optical absorption spectra of soda silicate slags containing various TiO_2 contents produced under the reducing condition

Table 1 Slag components, experimental conditions and ESR-measurements

Slag No.	Components (mol%)			P_{O_2} atm.	g-factor	intensity arbitrary units
	Na ₂ O	SiO ₂	TiO ₂			
1	10	85	5	2.1×10^{-9}	1.924	3.07
2	10	85	5	2.1×10^{-7}	1.924	1.41
3	10	85	5	2.1×10^{-5}	1.925	1.23
4	10	85	5	2.1×10^{-3}	1.924	0.163
5	12.5	82.5	5	2.1×10^{-9}	1.922	1.87
6	15	80	5	2.1×10^{-9}	1.925	1.04
7	20	75	5	2.1×10^{-9}	1.923	0.989
8	27	68	5	2.1×10^{-9}		
9	31.7	63.3	5	2.1×10^{-9}	1.925	0.261
10	10	87	3	2.1×10^{-9}	1.924	1.91
11	10	80	10	2.1×10^{-9}	1.926	8.80
12	33	66	1	2.1×10^{-9}		
13	32.3	64.7	3	2.1×10^{-9}	1.923	0.169
14	30	60	10	2.1×10^{-9}		
15	26.7	53.3	20	2.1×10^{-9}	1.928	3.00
16	23.3	46.7	30	2.1×10^{-9}	1.931	4.81

$g=1.924$ and optical density of Peak 1 in $10Na_2O-85SiO_2-5TiO_2$ slags as a function of partial oxygen pressures (P_{O_2}). The intensity of resonance increases with decreasing partial oxygen pressure in the high P_{O_2} region, then it becomes almost constant in the middle region of P_{O_2} . In the low P_{O_2} region, the intensity increases abruptly as P_{O_2} decreases. As a function of SiO₂ content the intensity of resonance near $g=1.924$ and optical density of Peak 1 in the slags containing 5 mol% TiO₂ are shown in Fig. 6. It is found that the dependence of the resonance on SiO₂ content is similar

**Fig. 4** ESR spectra of soda silicate slags containing 5.0 mol% TiO₂ produced under reducing condition**Fig. 5** Intensity measurements of ESR and optical density of soda silicate slags containing 5.0 mol% TiO₂ as a function of P_{O_2} in preparing atmosphere**Fig. 6** Intensity measurements of ESR and optical density of soda silicate slags containing 5.0 mol% TiO₂ produced under reducing condition as a function of SiO₂ content

to that on P_{O_2} . Nearly constant intensity is observed at the SiO_2 content from about 60 to 70 mol%.

4. Discussion

As shown in Figs. 5 and 6, both optical absorption near $20,000\text{ cm}^{-1}$ and electron spin resonance near $g=1.924$ show the similar dependence on partial oxygen pressure in the experimental atmosphere and SiO_2 content in the slag, so that it is considered that these are attributed to the Ti^{3+} ion in the ligand field with a same symmetry.

A. Arafa and A. Bishay⁸⁾ observed optical absorption near $20,000\text{ cm}^{-1}$ having a shoulder near $13,000\text{ cm}^{-1}$ in B_2O_3 -CaO- TiO_2 glass which were produced under reducing condition. From ligand field considerations they concluded that optical absorption at about $20,000\text{ cm}^{-1}$ is assigned to the ${}^2T_{2g} \rightarrow {}^2E_g$ transition in an octahedral symmetry and the shoulder at $13,000\text{ cm}^{-1}$ may be the result of tetragonal distortion of the octahedron of ligand. Energy levels of d^1 electron of Ti^{3+} ions in an octahedral environment with tetragonal distortion are shown in Fig. 7. On the other hand Kurkjian and Peterson⁹⁾ observed similar results in TiO_2 - SiO_2 glasses and considered that Ti^{3+} ions are in an octahedral symmetry with tetragonal distortion.

Using the theoretical expression for g values which was calculated by Pryce^{12,13)}, the g values for the Ti^{3+} center in the tetragonally distorted octahedral symmetry are obtained as follows:

$$g_{||} = g_e - 8\lambda/\Delta_{oct} \quad (1)$$

$$g_{\perp} = g_e - 2\lambda/\delta_{tet} \quad (2)$$

where g_e is the g value of the free electron, Δ_{oct} and δ_{tet} are the energy splittings in Fig. 7, and $\lambda=154\text{ cm}^{-1}$ is the spin-orbit coupling constant for the Ti^{3+} ion.¹⁴⁾

In K_2O - TiO_2 glasses gamma irradiated at liquid-nitrogen temperature, Kim and Bray¹⁵⁾ observed the broad asymmetric spectrum ($g_{||}=1.89$ and $g_{\perp}=1.975$). They considered that Ti^{3+} ions in the glass are in an octahedral symmetry with tetragonal distortion.

The g values for the Ti^{3+} ion in this study can be discussed using equations (1) and (2). In $10Na_2O$ - $85SiO_2$ - $5TiO_2$ glass, the energy splittings of Δ_{oct} and δ_{tet} are assumed to be $\Delta_{oct}=22,000\text{ cm}^{-1}$ and $\delta_{tet}=4,000\text{ cm}^{-1}$, the values of $g_{||}$ and g_{\perp} are estimated to be 1.946 and 1.925 respectively. The value of Δ_{oct} is the peak position of optical absorption. The value of δ_{tet} is obtained from the consideration that the splitting energy of ${}^2B_{2g} \rightarrow {}^2E_g$ transition may be equal to the difference between ${}^2B_{1g}$ and ${}^2A_{1g}$ levels. The split of 2E_g level to these levels is considered to arise from Jahn-Teller effect.¹⁶⁾ Generally it is considered

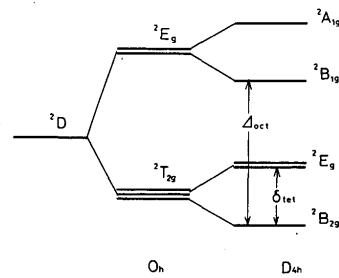


Fig. 7 Energy levels of Ti^{3+} ions in an octahedral environment with tetragonal distortion

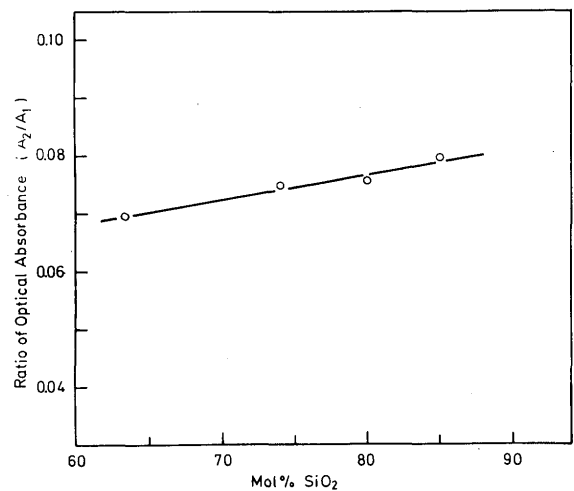


Fig. 8 Ratio of optical absorbances in Peak 2 and Peak 1 as a function of SiO_2 content

that the resonance due to g_{\perp} is stronger than that due to $g_{||}$. Further in glasses it is difficult to measure the resonance due to $g_{||}$ at room temperature. Therefore, it is reasonable to assign the $g=1.924$ resonance to g_{\perp} of Ti^{3+} ion in an octahedral symmetry with tetragonal distortion.

There appears to be somewhat correlation between optical absorption near $8,300\text{ cm}^{-1}$ (Peak 2) and resonance near $g=1.985$. In Fig. 8 the ratio of the optical absorbances in Peak 2 and Peak 1 is shown as a function of SiO_2 content of slags. This ratio increases as SiO_2 content increases, while in Fig. 4 resonance near $g=1.985$ is observed clearly at high SiO_2 content. These spectra may be attributed to Ti^{3+} ions in an octahedral environment with trigonal distortion¹⁷⁾ or in a tetragonal distortion.¹⁷⁾ For example, in the titanium (3) acetylacetonate, Ti^{3+} ions are known to be in an octahedral environment with trigonal distortion.¹⁸⁾ Besides, Ti^{3+} ion in a tetrahedral environment is unknown, but it is supported that this ion is able to be formed in the slags from the following relation¹⁷⁾;

$$J_{tet} = \frac{4}{9}\Delta_{oct} \quad (3)$$

where Δ_{tet} and Δ_{oct} are the crystal field splitting energies in tetrahedrally and octahedrally coordinated complexes. The relation is well established from crystal field theory. Substituting $\Delta_{oct}=20,000\text{ cm}^{-1}$ for this relation, $\Delta_{tet}\doteq 8,900\text{ cm}^{-1}$ is obtained and this value is fairly agree with the value of $8,300\text{ cm}^{-1}$. However, further investigation are necessitated to assign these spectra more completely.

It is well known that there are three kinds of oxygen in the silicate slags.¹⁹⁾ They are the bridged (O^0), non-bridged (O^-) and free (O^{2-}) oxygens. These ionic fractions in soda silicate slag were determined from molar refraction of oxygen by Iwamoto and Makino.²⁰⁾ According to their result, in soda silicate slags with high SiO_2 content the ionic fractions of O^{2-} and O^- are small as shown in Fig. 9. Therefore, it is expected that in the $Na_2O-SiO_2-TiO_2$ slags of this study the ionic fraction of O^{2-} is small in the high SiO_2 region.

Kim and Bray¹⁵⁾ observed two kinds of ESR spectra in K_2O-TiO_2 glasses gamma irradiated at liquid nitrogen temperature. As shown in Fig. 10 the broad asymmetric spectrum becomes small as K_2O content increases, while the sharp spectrum have a peak near 45 mol% K_2O . According to the dependence of the intensity on glass composition, it is considered that the broad and sharp spectra arise from a TiO_6 unit with a single nonbridging oxygen and a TiO_6 unit with two nonbridging oxygens, respectively. However, it is considered that nonbridging oxygen in K_2O-TiO_2 system is corresponded to free oxygen in Na_2O-SiO_2 system.

As shown in Fig. 6, the intensity of the resonance near $g=1.924$ shows an interesting dependence on the SiO_2 content. This suggests that the state of Ti^{3+} ions changes at about 80 mol% SiO_2 . Therefore, it is possible to think that Ti^{3+} ions are in the state of TiO_6 unit with two free oxygens at SiO_2 content less than 75 mol%, whereas in the region more than about 80 mol% SiO_2 Ti^{3+} ions are chiefly in the state of TiO_6 unit with a single free oxygen.

Taking into account the molecular orbital in TiO_6 unit, Δ_{oct} can be assigned to the transition energy of $\pi \rightarrow \sigma^*$. The magnitude of Δ_{oct} varies with the kind of center metal and ligand.²¹⁾ Because the formation of π -interaction of the ligand to the central metal ion elevates the energy level of π -orbital, Δ_{oct} becomes smaller as π -interaction becomes stronger. For example, oxygen atom of H_2O has no ability to form π -bond while that of OH^- is a weak π -donor.²¹⁾ Therefore Δ_{oct} is smaller in the case of H_2O ligand than that in the case of OH^- ligand. Spectrochemical

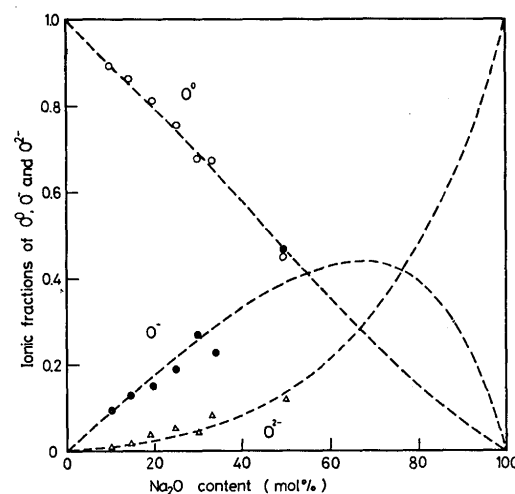


Fig. 9 Ionic fractions of O^0 , O^- , O^{2-} in the soda silicate slags (by N. Iwamoto and M. Makino²⁰⁾)

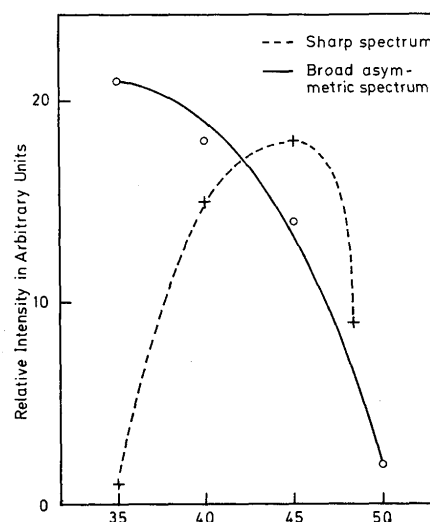


Fig. 10 Intensity measurement of ESR in the K_2O-SiO_2 glasses irradiated by γ -ray (by Y.M. Kim and P.J. Bray¹⁵⁾)

series of H_2O and OH^- indicated as following relation;²¹⁾



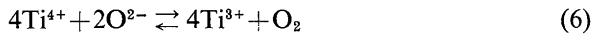
On the other hand, it is known that the free oxygen (O^{2-}) is a π -donor in $Na_2O-B_2O_3$ glasses.²²⁾ Therefore it is considered that there may be the following spectrochemical series between O^0 , O^- and O^{2-} in slags.



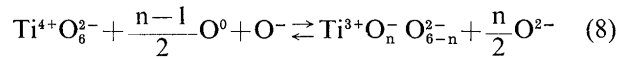
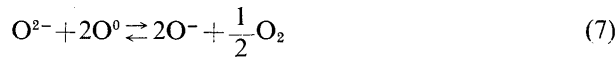
As shown in Fig. 11 the value of Δ_{oct} increases with increasing SiO_2 content. This suggests that the environment around Ti^{3+} ions is dependent upon SiO_2 content. As shown in the relation (5), as oxygen ligands of TiO_6 unit is replaced O^{2-} through O^- to O^0 , Δ_{oct} becomes larger by degrees. Therefore, it can

be considered that Ti^{3+} ions are chiefly in the form of $Ti^{3+} O_4^- O_2^{2-}$ in the not high SiO_2 region while these are chiefly in the form of $Ti^{3+} O_5^- O_2^{2-}$ in the high SiO_2 region. This consideration is supported by the result which are shown in Fig. 6. While, it is necessitated to investigate the relation (5) more fully.

In most cases, redox reaction for Ti^{4+} - Ti^{3+} equilibrium in oxide glasses can be written as follows;²³⁾



The dependence of Ti^{4+}/Ti^{3+} ratio on P_{O_2} can be explained using this equation. Therefore, the increase of Ti^{3+} ions with lowering P_{O_2} as shown in Fig. 5 can be explained using this equation. However, it has been indicated by some investigators^{23,24)} that the dependence of that ratio on glass composition can not be explained using this equation. For example, Holmquist expressed the redox reaction of iron ion using $Fe_2^{3+} O_{2x}^{4x-}$ complex ion. As discussed above, it is suggested that Ti^{3+} ion can be in the form of $Ti^{3+} O_4^- O_2^{2-}$ or $Ti^{3+} O_5^- O_2^{2-}$, so that the following redox equations can be suggested;



where n is predominantly five or four depending on glass composition. The dependence of Ti^{3+}/Ti^{4+} ratio on glass composition can be explained using equation (7), because the content of O^{2-} ion increases with decreasing SiO_2 content. As shown in Fig. 6, the relation of intensity of ESR of Ti^{3+} ion to SiO_2 content may be explained by this equation.

Dependence of the position of Peak 1 upon TiO_2 content is illustrated in Fig. 12. The position of Peak 1 shifts to higher wavenumber with increasing TiO_2 content, and then it saturates over a critical content of TiO_2 . The shift may arise from changing ionicity of oxygen around Ti^{3+} ion. After a critical content of TiO_2 , that may be not changeable.

Rao²⁵⁾ observed a minimum and a maximum in the dependence of the linear coefficient of thermal expansion and softening temperature on TiO_2 content in K_2O - SiO_2 - TiO_2 system. He suggested that the minimum and the maximum originates from the change of Ti^{3+} ion from predominantly fourfold to predominantly sixfold. However, the saturation of the position of Peak 1 can not arise from the coordination change of Ti^{3+} ions but from that of the ionicity of oxygens around these ions because the position depend on ligand field strength. In other words, it depends

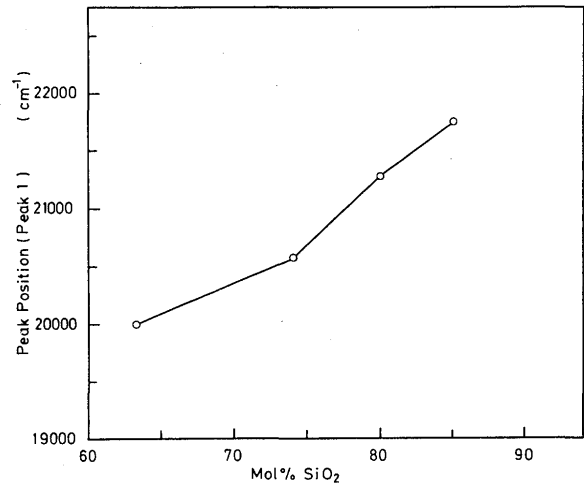


Fig. 11 Dependence of position of Peak 1 in optical absorption on a SiO_2 content

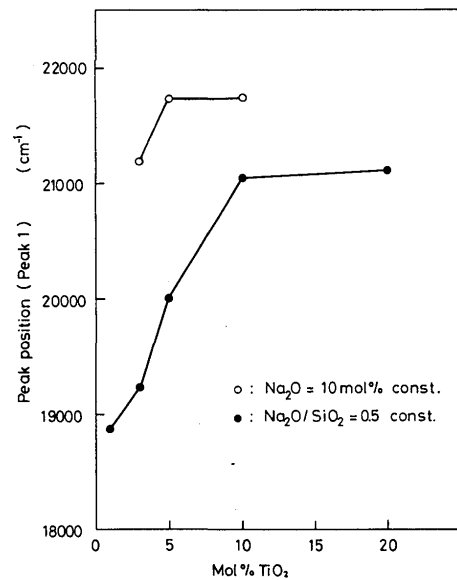


Fig. 12 Dependence of position of Peak 1 in optical absorption on a TiO_2 content

upon the kind of oxygen ions around Ti^{3+} ions.

4. Summary

In order to elucidate the effect of titanium ion in slag on welding process, state analysis of trivalent titanium ion in soda silicate slags containing TiO_2 , which were produced in the strong reducing condition ($P_{O_2} = 2.1 \times 10^{-9}$ atm), was performed by optical absorption and electron spin resonance spectroscopies. An absorption and a shoulder were observed at about $20,000 \text{ cm}^{-1}$ and $15,000 \text{ cm}^{-1}$, respectively. In the slags containing high silica content, another optical absorption was also observed near $8,300 \text{ cm}^{-1}$. An

ESR absorption was observed at $g=1.924$ and a shoulder appeared in the slags with high silica content.

It is indicated from these results that these absorptions and shoulders originate from Ti^{3+} ions and these ions are present in an octahedral environment with tetragonal or trigonal distortion, respectively. Dependences of the intensity of $g=1.924$ resonance and A_{oct} upon SiO_2 content suggest that Ti^{3+} ions can be in the form of $Ti^{3+} O_4^- O_2^{2-}$ unit at the content less than 80 mol% SiO_2 whereas in the form of $Ti^{3+} O_5^- O^{2-}$ unit at the higher SiO_2 content than 80 mol%. From the dependence of the peak position of the absorption near $20,000\text{ cm}^{-1}$ upon TiO_2 content it is indicated that the ionicity of oxygen around Ti^{3+} ions depends on TiO_2 content and it is attributed to the difference of oxygen species coordinated with Ti^{3+} ions.

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