State of Ti^{3+} ion in Soda-silicate Slags under Reducing Atmospheres†

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KEY WORDS: (State Analysis) (Slag) (Titanium)

The flux containing titania is weidely used in various welding processes and it is important to elucidate the behaviors of Ti ions in welding processes in the light of understanding slag-metal reactions. Recently, an attempt to transfer titanium from slag to weld metal is performed in order to improve various properties of weld metals.[1),2)] Further, it is indicated that titanium may be closely related with spolling property of slag from weld metal.

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 metalprefer to be in a lower valency states (Ti^{3+} or Ti^{2+}) than Ti^{4+}. From the observation of optical absorption, it is indicated that Ti^{3+} ions exist in glasses produced under reducing conditions.[3),4),5)] However, state of Ti^{3+} ion in slag, especially its coordination state, is not fully clarified as well as Ti^{4+} ion.[6)] In this study, state of Ti^{3+} ion in the slags of Na_2O-SiO_2-TiO_2 system was investigated by optical absorption and electron spin resonance (ESR) spectroscopies.

Specimen slags were prepared from analytical reagent Na_2CO_3, SiO_2 and TiO_2. After mixing these reagents in the desired ratios, they were preliminarily melted in platinum crucibles at 1600°C using an electric furnace. All preliminary melting were performed in air. Then, they were remelted and held for 3 hr at 1600°C under the CO/CO_2 mixed gas with $CO/CO_2 = 10$ and they were cooled in the top of the furnace. Glassy slags were polished for optical absorption measurement and pulverized for ESR measurement.

Figure 1 shows the result of optical absorption measurement. A strong absorption and a shoulder are observed near 500 nm (20000 cm^{-1}) and 750 nm (13300 cm^{-1}), respectively. In the spectrum obtained from slag A (5 mol% TiO_2, $Na_2O/SiO_2 = 10/85$), another absorption (absorption II) is observed near 1200 nm (8300 cm^{-1}). The intensity of the absorption near 500 nm (absorption I) increases with increasing SiO_2 content. In the aqueous solution containing Ti^{3+} ion, an absorption with a shoulder at 17400 cm^{-1} is observed at 20000 cm^{-1} and the absorption is originated from $[Ti(H_2O)_6]^{3+}$ ions[7)]. That is, the absorption is attributed to Ti^{3+} ions in octahedral coordination. The existence of the shoulder is due to Jahn-Teller effect and it is expected that the absorption is observed at the arithmetically averaged wave number of 500 nm (20000 cm^{-1}) and 750 nm (13300 cm^{-1}), that is, at about 600 nm (16650 cm^{-1}). From crystal field theory, following relation[8)] is well established;

$$\Delta_{tet} = \frac{4}{9}\Delta_{oct}$$

where Δ_{tet} and Δ_{oct} are crystal field splitting energies in tetrahedrally and octahedrally coordinated complexes. Applying the relation to the result in this study, Δ_{tet} becomes 7400 cm^{-1} (1350 nm). This value shows fairly a good agreement to that of absorption II, so that it is suggested that the absorption II is originated from tetrahedrally coordinated Ti^{3+} ions.

Figure 2 shows the ESR spectrum obtained from slag A. An absorption[4)] of Ti^{3+} ion in octahedral coordi-

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Transactions of JWRI is published by Welding Research Institute of Osaka University, Suita, Osaka, Japan

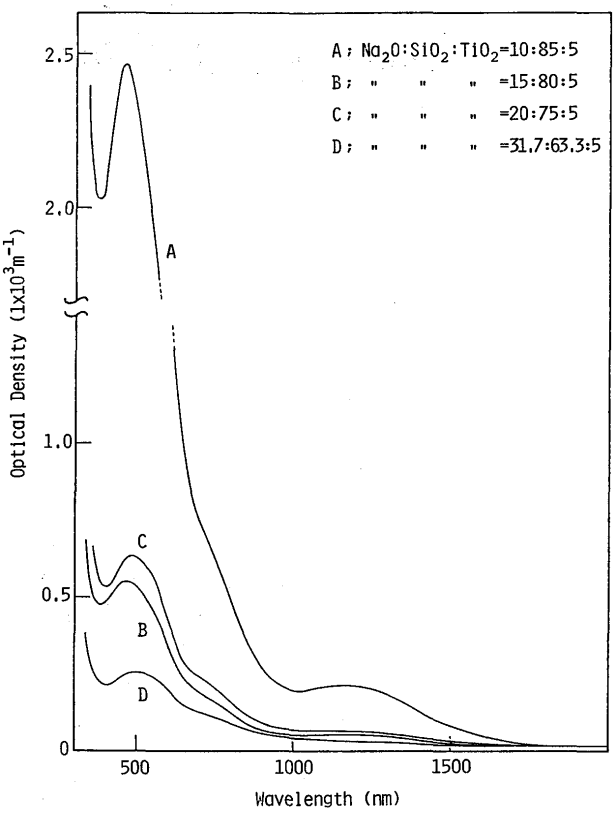

Fig. 1 The optical absorption spectra of Ti^{3+} ions in soda silicate glasses containing 5.0 mol% TiO_2 produced under the reducing condition (P_{CO}/P_{CO_2} = 10, 1600°C)

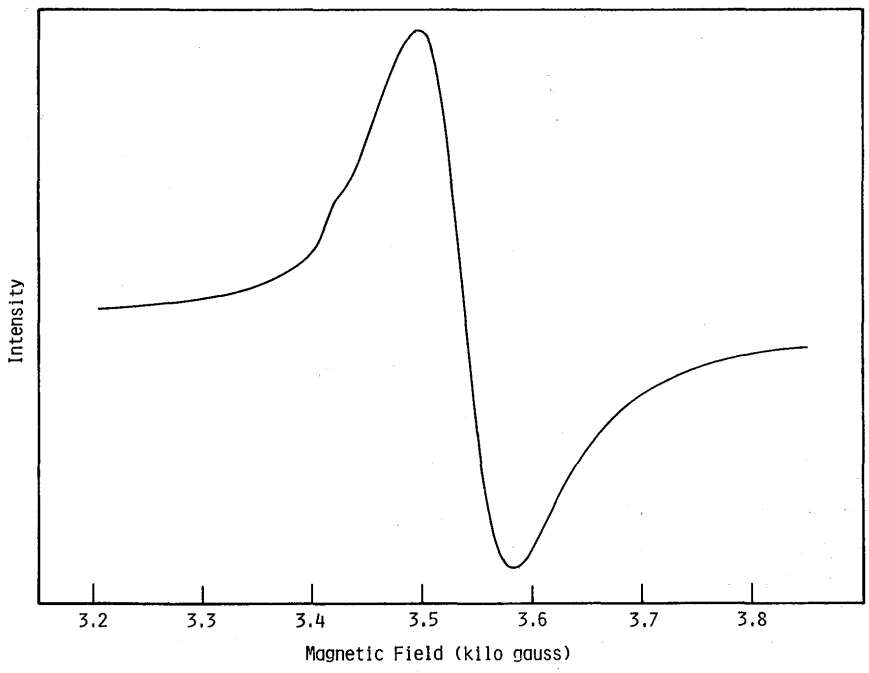

Fig. 2 The ESR spectrum of the glass (Na_2O/SiO_2 = 10/85, 5.0 mol% TiO_2) produced under the reducing condition (P_{CO}/P_{CO_2} = 10, 1600°C)

nation is observed near 3540 gauss and another absorption appears near 3420 gauss as a shoulder. It is anticipated that the latter absorption may be due to tetrahedrally coordinated Ti^{3+} ions. The detailed measurement of ESR is desired in near future.

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