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State Analysis of Hydrogen in Calcium Fluorosilicate Slag†

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KEY WORDS: (State Analysis) (Hydrogen) (Fluorosilicate Slag)

It is well known that hydrogen in steels or weld metals gives some harmful influences on their mechanical properties^{1), 2)}. In order to prevent hydrogen transferring from atmosphere to molten metal during steel refinement or welding, it is desired to develop the excellent slags (or flux) having very low permeability for hydrogen. In developing such excellent slags it is essential to clarify the state of hydrogen in slag. State of hydrogen in slag is also taken much interest from the standpoint of silicate structural theory including its basicity. It has been known that the addition of CaF_2 to slag is effective of decrease hydrogen and oxygen contents in weld metal^{3) 4)}. However, information on the interaction between hydrogen and fluorine ions in slag during metallurgical reaction still remains unclear. In this study, state of hydrogen in the calcium fluorosilicate slag was investigated by infrared absorption method.

All specimens were prepared from reagent grade CaCO_3 , SiO_2 and CaF_2 . These reagents were accurately weighed and mixed in an agate mortar and pestle. Specimen glasses were produced by melting in a platinum crucible in argon saturated water vapour. Partial pressure of saturated water vapour was fixed to be 0.128 atm. (97.3 mmHg) in every experiments, using water saturator which can regulate the temperature of water with the accuracy of $\pm 0.01^\circ\text{C}$. The mixed gas was led into a furnace as shown in Figure 1. After each specimen was held for 3 hr at the desired temperature, it was quenched by taking into air. Specimen glasses were polished by emery papers and buffed by aluminas powders. Infrared absorption spectra of these polished specimens were measured using a spectrometer of Hitachi 260 - 50 type.

Typical results are shown in Figures 2 and 3. Three absorptions were observed in the ranges of 2.85 to 3.10 μ ,

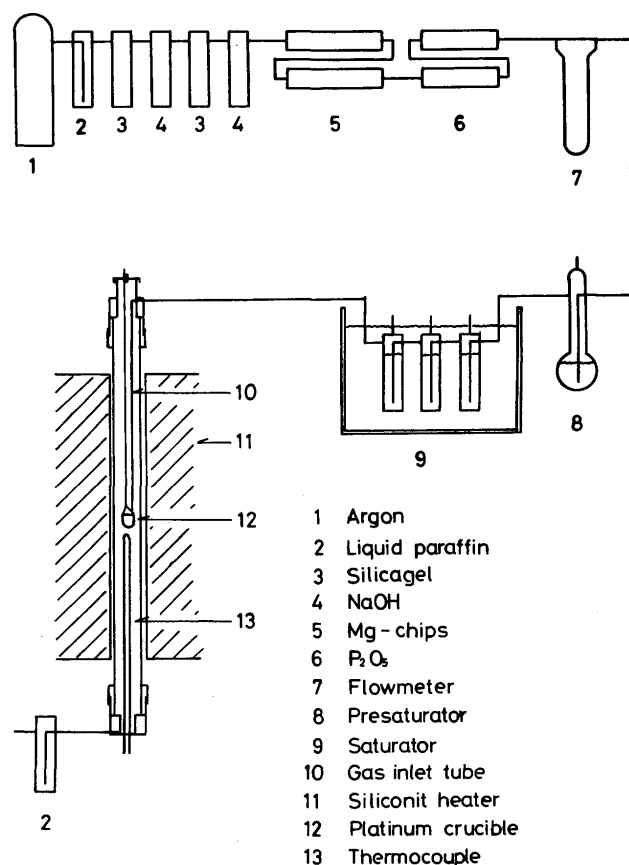


Fig. 1 Experimental Apparatus

3.30 to 3.58 μ and 4.15 to 4.33 μ , respectively. As shown in Fig. 2, infrared absorption spectra show two different patterns depending on additive CaF_2 content. According to Scholze⁵⁾, it is considered that the absorption with lowest wavelength (Band 1) is assigned to free hydroxyl

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and another two absorptions with intermediate and highest wavelengths (Band 2 and 3, respectively) originate from hydrogen-bonded hydroxyls [OH...O] and [OH O], respectively. That is, the intensity of band 1 has a tendency to decrease in the range of CaF₂ content less than about 5 mol% with increasing CaF₂ content whereas, in the range of CaF₂ content more than 5 mol%, it seems to increase with increasing CaF₂ content. Dependence of infrared absorption pattern upon CaF₂ content suggests that the quantities of three hydroxyls are related to the breaking behaviour of fluorine ion to Si-O bonds.

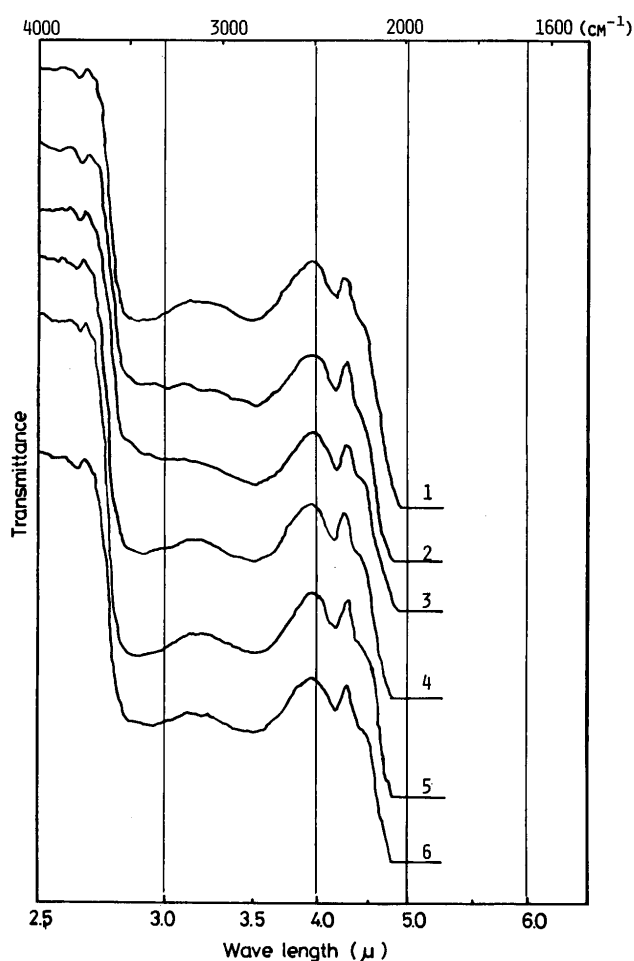


Fig. 2 Infrared absorption spectra of calcium fluorosilicate slags with CaO/SiO₂ = 1 (All slags were melted at 1600°C.)
(1) no CaF₂, (2) 3 mol% CaF₂, (3) 6 mol% CaF₂,
(4) 8 mol% CaF₂, (5) 10 mol% CaF₂, (6) 14 mol% CaF₂

In the previous results⁽⁶⁾⁻⁸⁾, it has been interpreted that the behavior of water vapour is amphoteric when it dissolves into molten slag. In other words, it is explained that dissolution form of water vapour into molten slag is closely related to bridged, non-bridged and free oxygens in acidic, basic and strong basic compositions, respectively.

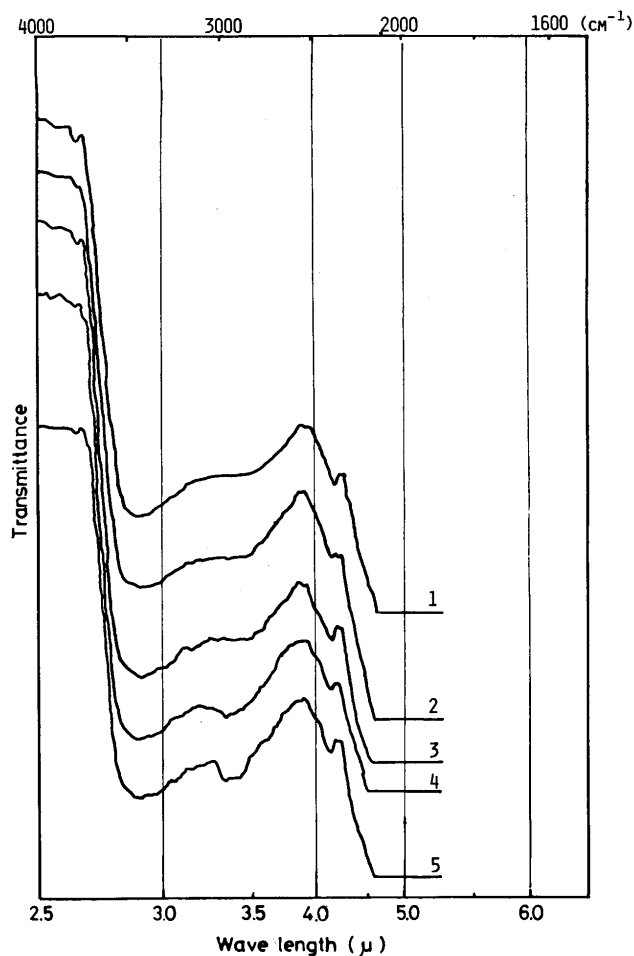
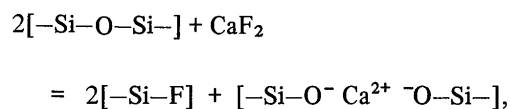
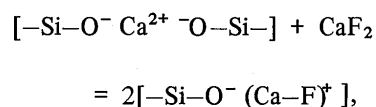


Fig. 3 Infrared absorption spectra of calcium fluorosilicate slags with 60 mol% SiO₂ (All slags were melted at 1600°C.)
(1) 40 mol% CaO, no CaF₂,
(2) 35 mol% CaO, 5 mol% CaF₂,
(3) 30 mol% CaO, 10 mol% CaF₂,
(4) 25 mol% CaO, 15 mol% CaF₂,
(5) 20 mol% CaO, 20 mol% CaF₂

If fluorine ion reacts to Si - O - Si bond by the reaction



the quantities of bridged and non-bridged oxygens varies before and after reaction. However, if fluorine ion reacts to Si-O⁻ bond by the reaction



the quantity of non-bridged oxygen and, of course, those of another two sorts of oxygens do not change before and after the reaction. Thus, behaviour of fluorine ion has an

important influence to the concentration of three sorts of oxygens in fluorosilicate. Conclusively, intensities of infrared absorptions due to three sorts of hydroxyls, especially bands 1 and 2, seem to be influenced by the difference of the reaction behaviours of fluorine ion to Si-O bond because three sorts of oxygens are closely related to the formations to of three sorts of hydroxyls. In further investigations, it is necessary to determine the states of three sorts of hydroxyls directly and relate these quantities to state of fluorine ion in fluorosilicate slag.

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