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REACTION BETWEEN WATER VAPOR AND MOLTEN ALUMINATE FLUXES

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Synopsis: Equilibrium and kinetics of water vapor dissolution into molten binary and ternary alkaline earth aluminates have been investigated by thermogravimetry. Hydroxyl capacities of various aluminates are obtained and the apparent diffusion coefficients of water in aluminates are evaluated from the experimental results. Hydroxyl capacities of CaO-Al_2O_3 system increase with increasing CaO contents. On the other hand, apparent diffusion coefficients decrease with increasing CaO contents in the aluminates. The relation between Hydroxyl capacities and other thermodynamic properties such as activities of components, sulphide capacities, phosphate capacities are considered. The values of the hydroxyl capacities and these properties are strongly related with the activity of the oxygen ion in the slags. On account of this, mechanisms of dissolution of water vapor into aluminate fluxes are discussed.

Key words: slag; secondary refining; water vapor; hydrogen; diffusion coefficient; oxygen ion; hydroxyl capacity; sulphide capacity; phosphate capacity.

1. Introduction

Alkaline earth aluminates are important fluxes in the secondary refining process with regard to desulphurization and deoxidation of liquid steel. This type flux, however, is predicted to have a high hydroxyl capacity, so it might be anxious that hydrogen would dissolve into liquid steel from water vapor in the atmosphere and water contained in fluxes. The studies concerning molten silicates have been reported by many investigators including us[1]~[22]. In our previous study, hydroxyl capacities and the apparent diffusion coefficients of water in the CaO-Al_2O_3 without and with MgO, SrO or BaO were determined by thermogravimetry[23]. Based on these experimental results, mechanisms of dissolution of water vapor and the relation between hydroxyl capacities and other thermodynamic properties are discussed in this paper.

2. Hydroxyl capacity

The solubilities of water vapor in liquid slags are proportional to the square root of partial pressures of water vapor at a given slag composition and temperature. This relationship has been confirmed by many investigators in the liquid silicates[1, 2, 3, 11, 15]. This relationship was also confirmed in liquid aluminates by Schwerdtfeger[24] et al. and our previous work[23] as shown in Fig.1.

Several capacities of slag have been proposed and defined[25, 26]. The hydroxyl capacity C_{OH} is defined by the following expression[27, 28].

$$C_{OH} = (\%H_2O)_S / P_{H_2O}^{1/2} \tag{1}$$

where, $(\%H_2O)_S$ and P_{H_2O} denote the solubility of water vapor and the partial pressure of water vapor, respectively. C_{OH} is independent of partial pressures of water vapor, but depends on the slag composition and temperature.

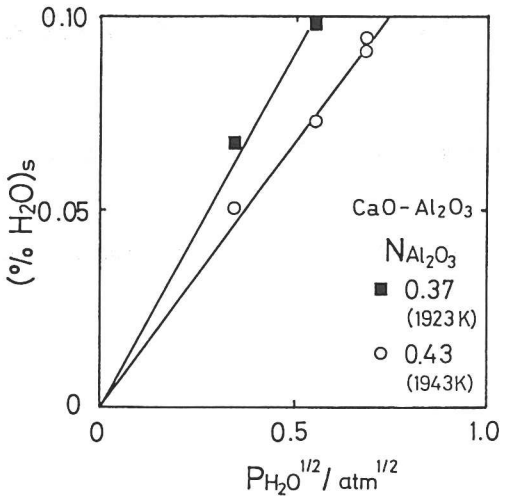

Fig. 1 Relation between water vapor solubility and square root of partial pressure of water vapor.

Hydroxyl capacities are shown in Fig.2 for $CaO\text{-}SiO_2$ melts[15, 16] in which minimum in hydroxyl capacity is observed at a certain CaO content.

Hydroxyl capacities of $CaO\text{-}Al_2O_3$ system are shown in Fig.3[23, 24]. From this figure, hydroxyl capacities of $CaO\text{-}Al_2O_3$ system increase monotonously with increasing CaO contents, over the experimental composition range at the temperatures below 1973K.

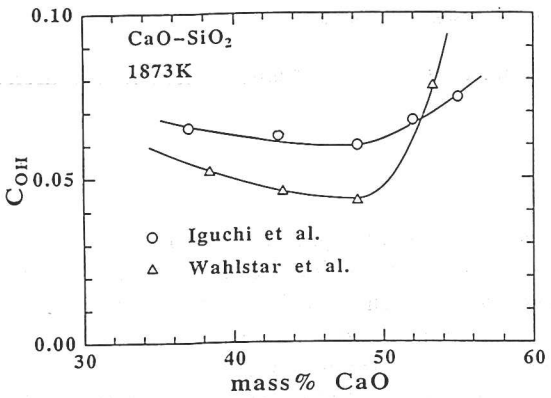

Fig. 2 Hydroxyl capacities of $CaO\text{-}SiO_2$ melts.

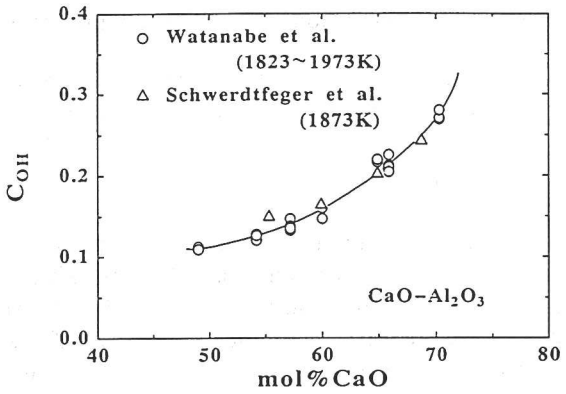

Fig. 3 Hydroxyl capacities of $CaO\text{-}Al_2O_3$ melts.

It has been reported that water vapor in liquid silicates exists as hydroxyl ion, hydroxyl radical or hydrogen bonded OH[5, 6, 7, 11]. Water vapor behaves in a fashion similar to an amphoteric oxide, and chemical reactions on the dissolution of water vapor into liquid slags are proposed as follows[1, 2]:

acid slag

$$\frac{1}{2}(O^0) + \frac{1}{2}H_2O(g) = (OH) \tag{2}$$

$$K_2 = \frac{a_{OH}}{P_{H_2O}^{1/2} \cdot a_{O^0}^{1/2}} \tag{3}$$

basic slag

$$(O^-) + \frac{1}{2}H_2O(g) = \frac{1}{2}(O^{2-}) + (OH) \tag{4}$$

$$K_4 = \frac{a_{OH} \cdot a_{O^{2-}}^{1/2}}{P_{H_2O}^{1/2} \cdot a_{O^-}} \tag{5}$$

or

$$(O^-) + \frac{1}{2}H_2O(g) = \frac{1}{2}(O^0) + (OH^-) \tag{6}$$

$$K_6 = \frac{a_{OH^-} \cdot a_{O^0}^{1/2}}{P_{H_2O}^{1/2} \cdot a_{O^-}} \tag{7}$$

Highly basic slag

$$\frac{1}{2}(O^{2-}) + \frac{1}{2}H_2O(g) = (OH^-) \tag{8}$$

$$K_8 = \frac{a_{OH^-}}{P_{H_2O}^{1/2} \cdot a_{O^{2-}}^{1/2}} \tag{9}$$

where, (O^0), (O^-) and (O^{2-}) are bridging oxygen, non bridging oxygen and free oxygen ion in slags, respectively.

The minimum in composition dependence of hydroxyl capacity of $CaO\text{-}SiO_2$ system is qualitatively explained as a summation of the effects of reactions (2)~(8).

Hydroxyl capacities of $CaO\text{-}Al_2O_3$ system increase monotonously with increasing CaO contents. From this tendency it seems that water vapor in $CaO\text{-}Al_2O_3$ slag is present in the form of free hydroxyl ion (OH^-) by the mechanism of Eq.(6) or Eq.(8).

Activities of the oxygen ions increase with increasing alkaline earth oxide contents. Accordingly, equilibrium concentration of the hydroxyl ion (OH^-) might increase.

3. Apparent diffusion coefficients of water in liquid aluminates

In our previous kinetic studies for the liquid silicates[21, 22] and aluminates[23], the rates of water vapor dissolution into molten slags were explained by diffusion of water in the bulk slag. The diffusing species so far have not been proved with regard to water in liquid slags. Consequently, the water content gradient in the bulk slag might be considered as a driving force of diffusion.

In these studies, as the bulk slag is shallow, diffusion in the finite media should be considered. In this case, the following equation is a solution to Fick's second law.

$$\frac{(\%H_2O) - (\%H_2O)_0}{(\%H_2O)_S - (\%H_2O)_0} = 1 - \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n-1)^2 \exp\{-(2n-1)^2\theta\}} \tag{10}$$

$$\text{where, } \theta = \pi^2 \cdot D_{H_2O} \cdot t/4l^2 \tag{11}$$

where, $(\%H_2O)_S$ is the solubility of water vapor in slag, D_{H_2O} is an apparent diffusion coefficient of water in slag [m^2/s] and is assumed not to depend on the water content, and l is slag depth [m].

Equation(10) was applied to analyze the experimental results. The values of $(\%H_2O)_S$ and D_{H_2O} were determined by the recursive least square method.

Apparent diffusion coefficients of water in $CaO\text{-}Al_2O_3$ slags[23] are shown in Fig.4. Apparent diffusion coefficients decrease with increasing CaO contents.

In alkali silicate slags, it is reported that the apparent diffusion coefficients of water in slags as a function of basicity change drastically when the basicity exceeds unity[22]. This drastic change is explained by the difference of the existing species of water depending on slag composition. As for the alkaline earth aluminates, hydroxyl capacities increased monotonously with increasing alkaline earth oxide contents and the apparent diffusion coefficients did not change drastically with the compositions. Accordingly, it seems that water vapor in alkaline earth aluminates is present in the form of free hydroxyl ion (OH^-) as described above.

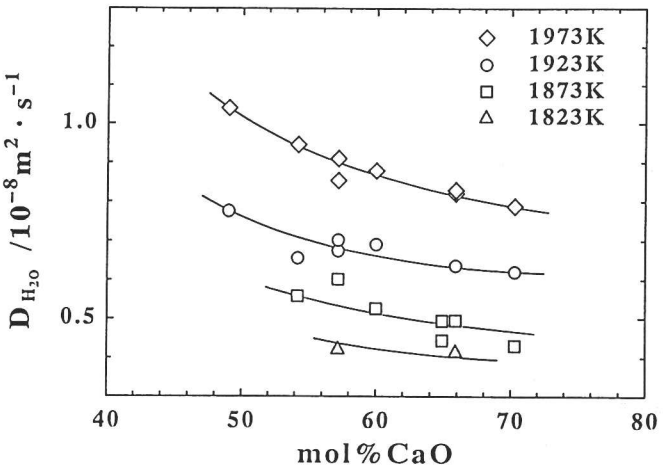

Fig. 4 Apparent diffusion coefficients of water in $CaO\text{-}Al_2O_3$ melts.

4. Comparison between hydroxyl capacities and sulfide capacities

Water vapor dissolves into liquid slag by the different reactions depending upon the slag system and composition. However, in highly basic slags such as $CaO\text{-}Al_2O_3$ system, water vapor dissolution could obey the reaction (8), as described above. On account of this, the hydroxyl capacities are expressed by the following equation.

$$C_{OH} = \frac{K_8 \cdot a_{O^{2-}}^{\frac{1}{2}}}{f_{OH^-}} \tag{12}$$

Sulphide capacities are also important properties of slags in the refining processes of steel. The dissolution reaction of sulphur into slag is expressed as Eq.(13). And the sulphide capacity $C_{S^{2-}}$ is defined by Eq.(15). Sulphide capacities are also strongly related with the activity of the oxygen ion in the slags, as shown in Eq.(15). Accordingly, the correlation between hydroxyl capacities and sulphide capacities are expected.

$$\frac{1}{2}S_2(g) + (O^{2-}) = (S^{2-}) + \frac{1}{2}O_2(g) \tag{13}$$

$$K_{13} = \frac{P_{O_2}^{\frac{1}{2}} \cdot a_{S^{2-}}}{P_{S_2}^{\frac{1}{2}} \cdot a_{O^{2-}}} \tag{14}$$

$$C_{S^{2-}} = (\text{mass\% } S^{2-}) \cdot (P_{O_2}/P_{S_2})^{\frac{1}{2}} = \frac{K_{13} \cdot a_{O^{2-}}}{f_{S^{2-}}} \tag{15}$$

The relations between hydroxyl capacities[23] and sulphide capacities for $CaO\text{-}Al_2O_3$[26, 29] systems are plotted in Fig.5. Figure 5 shows the linear correlations between hydroxyl capacities and sulphide capacities of the $CaO\text{-}Al_2O_3$ system.

The triangle in Fig.5 shows the slope obtained by considering that f_{OH^-} in Eq.(12) and $f_{S^{2-}}$ in Eq.(15) are constant.

5. Comparison between hydroxyl capacities and phosphate capacities

The dissolution reaction of phosphorus into slag is expressed and phosphate capacity is defined as follows:

$$\frac{1}{2}P_2(g) + \frac{5}{4}O_2(g) + \frac{3}{2}(O^{2-}) = (PO_4^{3-}) \tag{16}$$

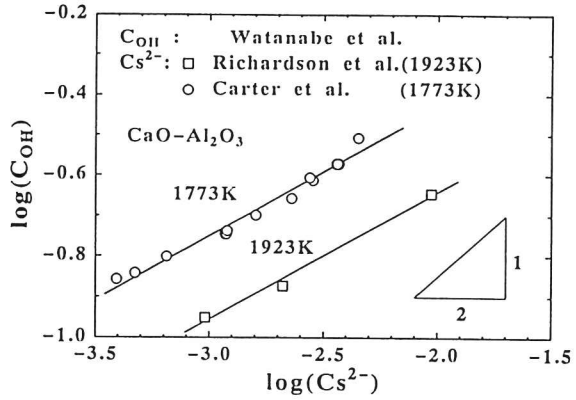

Fig. 5 Relation between hydroxyl capacities and sulphide capacities of $CaO-Al_2O_3$ system.

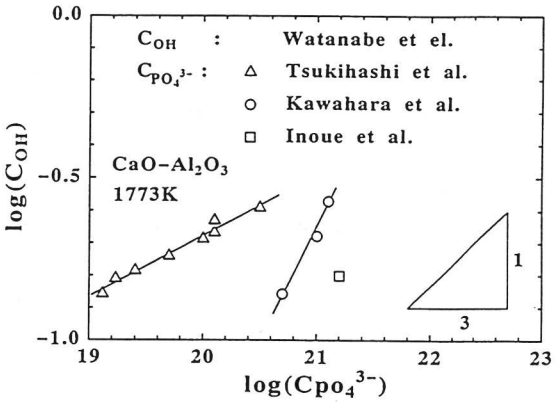

Fig. 6 Relation between hydroxyl capacities and phosphate capacities of $CaO-Al_2O_3$ system.

$$K_{16} = \frac{a_{PO_4^{3-}}}{P_{P_2}^{\frac{1}{2}} \cdot P_{O_2}^{\frac{5}{4}} \cdot a_{O^{2-}}^{\frac{3}{2}}} \tag{17}$$

$$C_{PO_4^{3-}} = (\text{mass\% } PO_4^{3-})/(P_{P_2}^{\frac{1}{2}} \cdot P_{O_2}^{\frac{5}{4}}) = \frac{K_{16} \cdot a_{O^{2-}}^{\frac{3}{2}}}{f_{PO_4^{3-}}} \tag{18}$$

The correlation between hydroxyl capacities and phosphate capacities are also expected. Figure 6 shows the correlations between hydroxyl capacities[23] and phosphate capacities[31, 32, 33] of the $CaO-Al_2O_3$ system.

But, there is a possibility that dissolution of water vapor, sulphur or phosphorus into liquid slags is affected not only by the activity of oxygen ion but also by the composition dependency of activity coefficients of the species dissolved in slags. Therefore, more precise and wider composition range experiments, and further considerations will be required.

6. Conclusion

1. Dissolution mechanisms of water vapor into liquid slags are complicated depending upon the slag system and compositions. But based on our previous experimental results, hydroxyl capacities and apparent diffusion coefficients of water in $CaO-Al_2O_3$ melts could be simply explained as the dissolution of water vapor in the form of free hydroxyl ion.

2. Good correlations between hydroxyl capacities and sulphide capacities or phosphate capacities are obtained in $CaO-Al_2O_3$ slags at a certain slag composition and at a given temperature range.

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