

# Effects of Slag Compositions on the Rate of Methane–Steam Reaction

Taihei SHIMADA, Vladimir KOCHURA,<sup>1)</sup> Tomohiro AKIYAMA,<sup>2)</sup> Eiki KASAI and Jun-ichiro YAGI

Institute for Advanced Materials Processing, Tohoku University, 2-1-1 Katahira, Aoba-ku, Sendai 980-8577 Japan.

1) Department of Ore Thermal Processes and Low Waste Technology, Donetsk State Technical University, 58 Artyom Street, Donetsk 83000, Ukraine.

2) Department of Chemical Engineering, Graduate School of Engineering, Osaka Prefecture University, 1-1 Gakuen-cho, Sakai 599-8531 Japan.

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For the effective heat recovery from molten slag by utilizing a chemical reaction, rates of the methane–steam reaction on the slag surface were studied for thirteen slag samples, in which effects of mass ratio of CaO to SiO<sub>2</sub> (CaO/SiO<sub>2</sub> ratio), and concentrations of wustite (FeO) and sulfur in slag on the reaction rate were systematically examined in the slag temperature range from 1 473 to 1 823 K.

The results showed that the higher CaO/SiO<sub>2</sub> ratio, meaning the weaker network structure of molten slag, gives rise to the higher rate of methane–steam reaction. In contrast, the FeO addition to slag brings about the lower reaction rate than that for the slag without FeO, indicating the inhibitory effect of FeO on the reaction. The higher FeO concentration proportionally provides the stronger inhibitory effect over the slag temperature of 1 773 K, while it is independent on both of the slag temperature and the FeO concentration under the temperature of 1 673 K. The results also revealed that the sulfur contained in slag has the inhibitory effect on the methane–steam reaction, which is much larger than the equi-mass of FeO over 1 673 K. This inhibitory effect of sulfur increases with increasing the sulfur concentration from 0.5 to 1.0 mass%, whereas it is insignificantly enhanced by the further increase in the sulfur concentration.

KEY WORDS: heat recovery; molten slag; methane–steam reaction; slag composition; mass ratio of CaO to SiO<sub>2</sub>; FeO; sulfur.

## 1. Introduction

Iron- and steel-making is well known as an energy-intensive process. Although some technologies have been introduced to use energy efficiently, the recovery ratio of outflow heat is still 17.5%<sup>1)</sup> in enthalpy basis and 25.3% in exergy basis in the typical steelworks. Molten slag is inevitably discharged from the steel-making industry as by-product at higher temperature than 1 600 K and over 30 Mt a year in amount. In spite of the high potential of the molten slag as a valuable energy source, the sensible heat is currently emitted into atmosphere without any recovery due to the technical difficulties arising from its high temperature. Therefore, the molten slag has been recognized as a main source of the waste heat in the industry.

In 1980's, the thermal energy of blast furnace (BF) slag was attempted to be recovered as a Japanese national project.<sup>2)</sup> In the process, sensible heat of hot air was utilized to recover the waste heat of molten slag, while the process has never been put to practical use. In contrast to sensible heat, utilization of heat of reaction is greatly promising for the effective heat recovery. It is quite advantageous in energy storage and/or transportation without heat loss,<sup>3,4)</sup> and is further attractive from the viewpoint of combining the steel industry with other industries.<sup>5)</sup> In the previous paper,<sup>6)</sup> the authors proposed a process for the heat recovery from

molten slag by utilizing a chemical reaction. In the process, an endothermic reaction between methane and steam (Eq. (1)) was selected as the reaction due to its sufficiently large enthalpy change, wide utilization of product gases of hydrogen and carbon monoxide in the other industries, and so on.

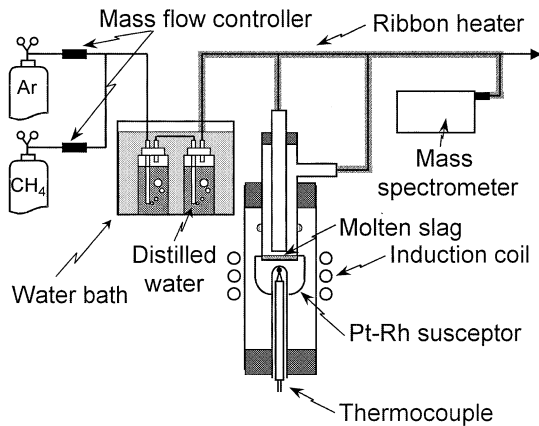


We experimentally verified that the reaction of Eq. (1) proceeds on the surface of molten slag, and then measured the reaction rates for three different BF slag samples. Although the experimental results revealed that the slag containing sulfur provides a relatively small reaction rate, a systematic investigation on the effects has never been done.

Blast furnace slag mainly consists of SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, CaO and MgO, the total amount of which reaches more than 95 mass%. Minor components of S, TiO<sub>2</sub>, MnO and FeO are also contained in the slag. The slag compositions as well as the slag basicity are strongly dependent on the compositions of iron ore, coke, flux, and so on, in other words, the operating conditions of the blast furnace. Hence, the aim of this paper is to study systematically the effects of slag compositions, in particular, mass ratio of CaO to SiO<sub>2</sub> (CaO/SiO<sub>2</sub> ratio), and concentrations of wustite (FeO) and sulfur, on the rate of methane–steam reaction on molten slag surface.

**Table 1.** Chemical compositions of slag samples used.

Sample	mass%						
	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	CaO	MgO	FeO	S	CaO/SiO <sub>2</sub>
#1	40.0	15.0	40.0	5.0	0	0	1.0
#2	38.1	15.0	41.9	5.0	0	0	1.1
#3	36.4	15.0	43.6	5.0	0	0	1.2
#4	35.6	15.0	44.4	5.0	0	0	1.25
#5	34.8	15.0	45.2	5.0	0	0	1.3
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#6	36.1	15.0	43.4	5.0	0.5	0	1.2
#7	35.9	15.0	43.1	5.0	1.0	0	1.2
#8	35.7	15.0	42.8	5.0	1.5	0	1.2
#9	35.5	15.0	42.5	5.0	2.0	0	1.2
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#10	36.1	15.0	43.4	5.0	0	0.5	1.2
#11	35.9	15.0	43.1	5.0	0	1.0	1.2
#12	35.7	15.0	42.8	5.0	0	1.5	1.2
#13	35.5	15.0	42.5	5.0	0	2.0	1.2



**Fig. 1.** Schematic diagram of apparatus.

**2. Experimental**

**2.1. Slag Samples**

Thirteen slag samples synthesized in the different compositions were employed. Chemical reagents of SiO<sub>2</sub>, Ca(OH)<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, MgO, Fe<sub>2</sub>O<sub>3</sub> and S were used as raw materials. They were weighed out to make the individual slags having compositions as listed in **Table 1**, and were mixed in a Pt crucible. The mixture was heated for two hours at the temperature 150 K above the liquidus temperature estimated from the phase diagram.<sup>7)</sup> The melted slag was subsequently thrown into water, and then crushed to make the size under 1 mm.

For all the slags, the compositions of Al<sub>2</sub>O<sub>3</sub> and MgO were kept constant at 15.0 and 5.0 mass%, respectively. Slags #1 to #5 were prepared to make different CaO/SiO<sub>2</sub> ratios in the range of 1.0 to 1.3. The concentration of FeO was varied from 0.5 to 2.0 mass% in slags #6 to #9, keeping CaO/SiO<sub>2</sub> ratio at the constant value of 1.2. The concentration of sulfur was also varied from 0.5 to 2.0 mass% in slags #10 to #13, keeping CaO/SiO<sub>2</sub> ratio at 1.2.

**2.2. Apparatus and Procedure**

**Figure 1** shows a schematic diagram of the experimental apparatus employed. A Pt-Rh susceptor of 15 mm diameter was machined to have a well of 13 mm in diameter and 3 mm in depth at the top. It was also machined to have a holl at the bottom, where an alumina tube was inserted to keep the susceptor in the center of induction coil. The susceptor temperature was measured by a thermocouple introduced through the alumina tube to a height about 3 mm

below the bottom of the well. In the present experiments, the susceptor temperature was employed as the slag temperature. A 10 mm i.d. translucent (highly dense) alumina tube one end of which was connected to a fused silica tube was set in the well. The susceptor was inductively heated at 1773 K, and subsequently 0.8 g of the slag sample was dropped into the well from the top of the silica tube. At each run, the surface of the susceptor was confirmed to be covered with the melted slag. After the experiments, degradation of the translucent alumina tube by the slag was never observed. Preliminary experiments revealed that the reaction rate on the surface of alumina tube was insignificant. Therefore, in the present experimental setup, the reaction area was limited only to the slag surface.

After keeping the slag temperature at the prescribed one, a mixed gas of Ar, CH<sub>4</sub> and H<sub>2</sub>O was blown to the slag surface through a 4 mm i.d. alumina tube inserted from the top of the silica tube. A gas mixture of Ar and CH<sub>4</sub>, each flow rate of which was controlled by a mass flow controller, was bubbled into distilled water in two bottles placed in a hot water bath to add water vapor. The concentration of H<sub>2</sub>O in the mixed gas was controlled by the temperature of the water bath. The inlet and outlet gas tubes were heated at around 420 K to prevent water condensation. Based on the previous experimental results,<sup>6)</sup> in the present experiments, the total flow rate of the mixed gas was fixed at 1.25 × 10<sup>-5</sup> m<sup>3</sup>/s. The gas composition was also set at the constant one; 50 (mol%) of Ar, 10 of CH<sub>4</sub> and 40 of H<sub>2</sub>O. The slag temperature was varied from 1473 to 1823 K.

Gas analyses were conducted for the gas species of H<sub>2</sub>, CH<sub>4</sub>, H<sub>2</sub>O, CO, Ar, CO<sub>2</sub> and O<sub>2</sub>. The molar fractions of the gas components in the inlet and outlet gases were alternately measured for 5 and 10 min, respectively, with a mass spectrometer for several times during each run. Scanning cycle was set at 15 s. The outlet gas composition was almost constant more than 5 min. The difference between concentrations of the inlet gases before and after experiment was less than 0.1 mol% of the original one. Disappearance rate of the *i* component, *R<sub>i</sub><sup>\*</sup>* (mol/s m<sup>2</sup>), was calculated from the measured fraction by the following equation;

$$R_i^* = \frac{P(x_i^{in} F^{in} - x_i^{out} F^{out})}{RT_g A} \dots\dots\dots(2)$$

where *P* is pressure (Pa), *x<sub>i</sub><sup>in</sup>* and *x<sub>i</sub><sup>out</sup>* are molar fractions (-) of *i* component in the inlet and outlet gases, respectively, *F<sup>in</sup>* and *F<sup>out</sup>* are volumetric flow rates (m<sup>3</sup>/s) of the inlet and outlet gases, respectively, *R* is gas constant (J/mol K), *A* is reaction area (m<sup>2</sup>) and *T<sub>g</sub>* is gas temperature (K). The outlet gas flow rate, *F<sup>out</sup>*, was calculated by Eq. (3) where it was assumed that Ar never takes part in the reaction.

$$F^{out} = \frac{x_{Ar}^{in}}{x_{Ar}^{out}} F^{in} \dots\dots\dots(3)$$

The disappearance rate of CH<sub>4</sub> was applied to the reaction rate of Eq. (1), since the carbon deposition was not detected, the CO<sub>2</sub> and O<sub>2</sub> concentrations in the outlet gas were negligibly small, and the stoichiometric relation between the disappearance rates of CH<sub>4</sub> and H<sub>2</sub>O, and the formation

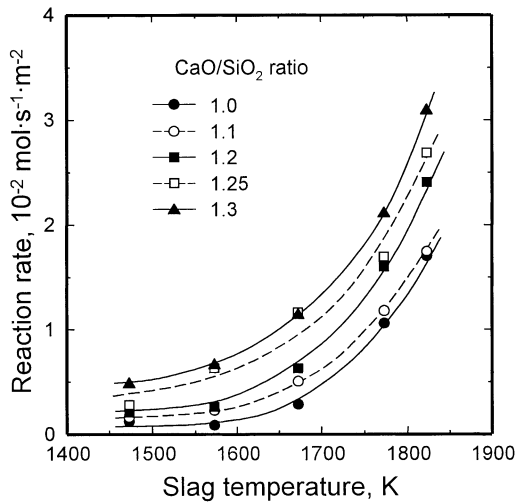


Fig. 2. Changes in rate of methane–steam reaction with slag temperature for slags having different CaO/SiO<sub>2</sub> ratios.

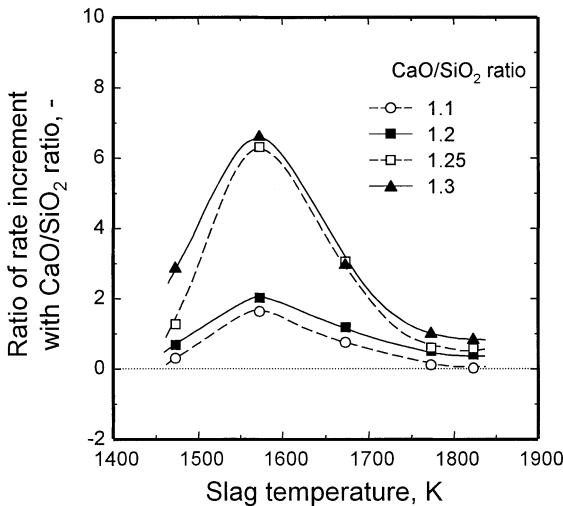


Fig. 3. Plots of ratio of rate increment with CaO/SiO<sub>2</sub> ratio against slag temperature.

rates of H<sub>2</sub> and CO nearly satisfied the Eq. (1) in any experiments.

3. Results and Discussions

3.1. Effect of Mass Ratio of CaO to SiO<sub>2</sub> in Slag on the Methane–Steam Reaction Rate

Effect of CaO/SiO<sub>2</sub> ratio on the rate of methane–steam reaction was examined. Figure 2 shows changes in the reaction rate with slag temperature for slags #1 to #5. The slag having a higher CaO/SiO<sub>2</sub> ratio gives rise to a larger reaction rate within the slag temperature range examined. It is also seen that the reaction rate begins to increase significantly above the slag temperature of 1600 K, exhibiting a slight increase in the lower temperature range. Further, the trend of the change seems to be similar for one another. In Fig. 3, the ratios of rate increment with CaO/SiO<sub>2</sub> ratio,  $r_{CaO/SiO_2}$ , to the reaction rate for the slag having the CaO/SiO<sub>2</sub> ratio of 1.0 are plotted against slag temperature. Here,  $r_{CaO/SiO_2}$  is defined as

Table 2. Values of specific coefficient,  $\alpha_i$ , used.<sup>8)</sup>

Component	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>			CaO	MgO
		1673 K	1773 K	1823 K		
$\alpha_i$	1.48	1.02	1.08	1.09	1.53	1.51

$$r_{CaO/SiO_2} = \frac{R_i^{*CaO/SiO_2} - R_{1.0}^{*CaO/SiO_2}}{R_{1.0}^{*CaO/SiO_2}} \dots\dots\dots(4)$$

where,  $R_i^{*CaO/SiO_2}$  and  $R_{1.0}^{*CaO/SiO_2}$  are the reaction rates for the slags having CaO/SiO<sub>2</sub> ratios of  $i$  and 1.0 at a given temperature, respectively. The ratio,  $r_{CaO/SiO_2}$ , increases with increasing slag temperature in the lower temperature region, and reaches a maximum at the temperature of 1573 K. After that, it decreases until the temperature goes up to 1773 K. With the further increase of the slag temperature,  $r_{CaO/SiO_2}$  also decreases, while the decrement is relatively small. This results reveals that the effect of CaO/SiO<sub>2</sub> ratio on the rate increase is significant around the slag temperature of 1573 K, especially for the CaO/SiO<sub>2</sub> ratios of 1.25 and 1.3. At the higher slag temperature than 1773 K, the effect of CaO/SiO<sub>2</sub> ratio for the rate increase is almost proportional to the ratio though the value  $r_{CaO/SiO_2}$  of is less than 1.0.

When CaO/SiO<sub>2</sub> ratio increases, the liquidus temperature goes up within the CaO/SiO<sub>2</sub> ratio range examined.<sup>7)</sup> Reflecting the change, the physicochemical properties of slag such as viscosity also change with CaO/SiO<sub>2</sub> ratio. Iida *et al.*<sup>8)</sup> presented an empirical viscosity equation for blast furnace type slags by introducing “network parameter”, which represents the state of network structure of slag, that is, the extent of strength and expansion of the network. They related the network parameter to the basicity index in a form of inverse proportion. The basicity index which they employed,  $Bi^*$ , is given by;

$$Bi^* = \frac{\sum (\alpha_i W_i)_B}{\sum (\alpha_i W_i)_A} \dots\dots\dots(5)$$

where  $\alpha_i$  and  $W_i$  are specific coefficient (–) and mass percent (%) of the  $i$  component in slag, respectively, and the subscripts A and B mean acidic oxide (SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub>) and basic oxide (CaO and MgO), respectively. In Table 2, the values of  $\alpha_i$  employed are listed.<sup>8)</sup> Figure 4 shows the semi logarithmic plots of the reaction rate against the reciprocal basicity index for the slag temperatures from 1673 to 1823 K. The logarithmic value of the reaction rate straightly decreases with increasing the reciprocal basicity index. This means that the slag having the weaker state of network structure gives rise to the higher rate of the methane–steam reaction. In general, the network structure of silicate anion in molten slag is broken by basic component added,<sup>9)</sup> resulting in the decrease in strength of the network structure. Therefore, the increase of CaO/SiO<sub>2</sub> ratio provides the increase of calcium cation bonding the silicate anions. Although the detailed evaluation to clarify the reaction mechanism has never been conducted in the present study, the above-mentioned results suggest that the calcium plays a role of a site for the methane–steam reaction.

The figure also shows that the slope of the straight line becomes more gradual with increasing the slag tempera-

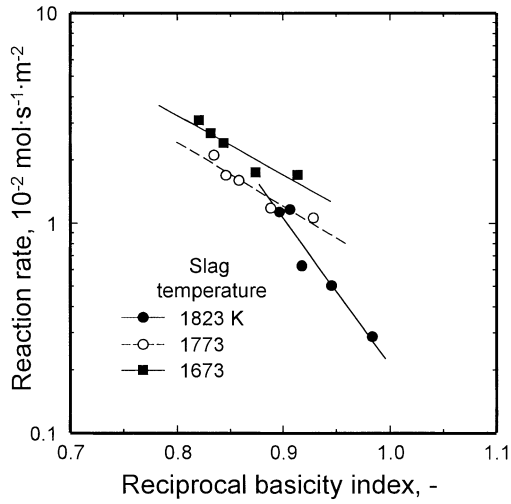


Fig. 4. Semi logarithmic plots of reaction rate against reciprocal basicity index.

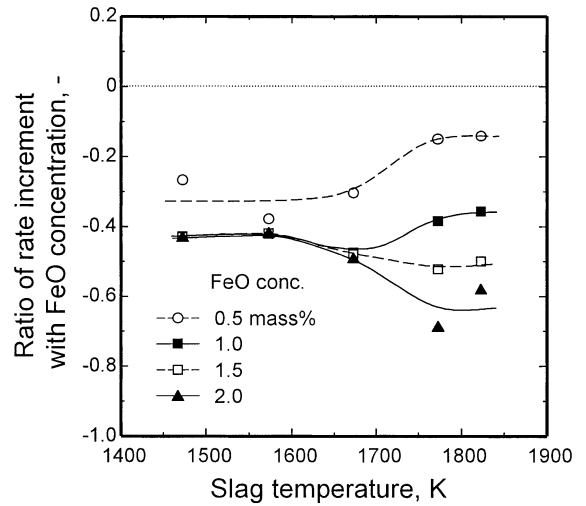


Fig. 6. Plots of ratio of rate increment with FeO concentration against slag temperature.

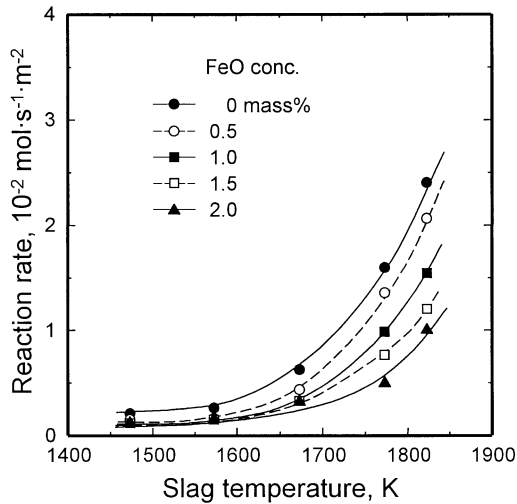


Fig. 5. Changes in rate of methane–steam reaction with slag temperature for slags having different concentrations of FeO in slag.

ture. This result indicates that the dependence of the reaction rate on the network structure becomes smaller with increasing the slag temperature.

### 3.2. Effect of FeO Concentration on the Methane–Steam Reaction Rate

Rate of methane–steam reaction was measured for the slags having different concentrations of FeO. Figure 5 shows changes in the reaction rate with slag temperature for slags #6 to #9. The change for slag #3, which has 0 mass% FeO, is also drawn in the same figure as a reference. It is apparent from the figure that the FeO addition to slag brings about the lower reaction rate than that for the slag without FeO. The reaction rate increases with increasing the slag temperature as is the case for the CaO/SiO<sub>2</sub> ratio, while the extent of the rate increase becomes smaller with increasing the FeO concentration above the slag temperature of 1 600 K. Here, the ratio of rate increment with FeO concentration,  $r_{\text{FeO}}$ , to the reaction rate for the slag without containing FeO (slag #3) was defined in the same manner for  $r_{\text{CaO/SiO}_2}$  as follows;

$$r_{\text{FeO}} = \frac{R_i^{*\text{FeO}} - R_0^{*\text{FeO}}}{R_0^{*\text{FeO}}} \dots\dots\dots(6)$$

where,  $R_i^{*\text{FeO}}$  and  $R_0^{*\text{FeO}}$  are the reaction rates at the respective FeO concentrations of  $i$  and 0 mass% at a given temperature. In Fig. 6, changes in  $r_{\text{FeO}}$  with slag temperature are shown. The slags containing FeO provide negative values of  $r_{\text{FeO}}$ , clearly indicating that FeO has an inhibitory influence on the methane–steam reaction. In the slag temperature range from 1 473 to 1 673 K,  $r_{\text{FeO}}$  are almost same for one another, whereas that for 0.5 mass% FeO is slightly larger. This means that the inhibitory effect of FeO is equivalent without depending on the slag temperature as well as the FeO concentration. At the slag temperature of 1 773 K, the smaller values of  $r_{\text{FeO}}$  are obtained in proportion to the FeO concentration. These values keep almost constant with increasing the temperature to 1 823 K, indicating that the inhibitory effect of FeO occurs in dependence on the FeO concentration, but not on the temperature, above the slag temperature of 1 773 K.

FeO is also a basic component, thus it plays a same role as CaO to break the network structure of silicate anion in molten slag.<sup>9)</sup> However, the experimental results indicate that the iron ion in molten slag might never act as a site on the reaction, which is an opposite trend to the calcium iron.

### 3.3. Effect of Sulfur Concentration on the Methane–Steam Reaction Rate

Figure 7 depicts changes in the rate of methane–steam reaction with slag temperature for the slags having different sulfur concentrations (slags #10 to #13). The reaction rates for the slag #3 are also plotted in the same figure as a reference. Similarly to FeO, sulfur contained in slag provides the reduction in the reaction rate, except at the slag temperature lower than 1 673 K for the sulfur concentration of 0.5 mass%. Compared with Fig. 5, in the higher temperature range than 1 673 K, the reaction rate for 0.5 mass% S is equivalent to that for 0.5 mass% FeO. On the other hand, obviously, the sulfur more than 1.0 mass% gives the rate reduction much larger than the equi-mass of FeO. Figure 8 represents plots of  $r_s$ , which is defined by Eq. (7), against

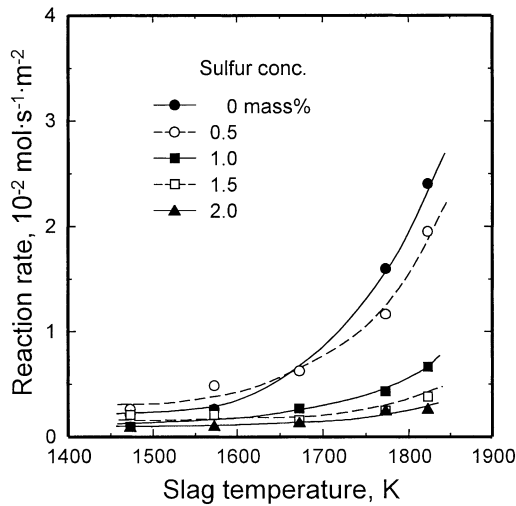


Fig. 7. Changes in rate of methane–steam reaction with slag temperature for slags having different sulfur concentrations in slag.

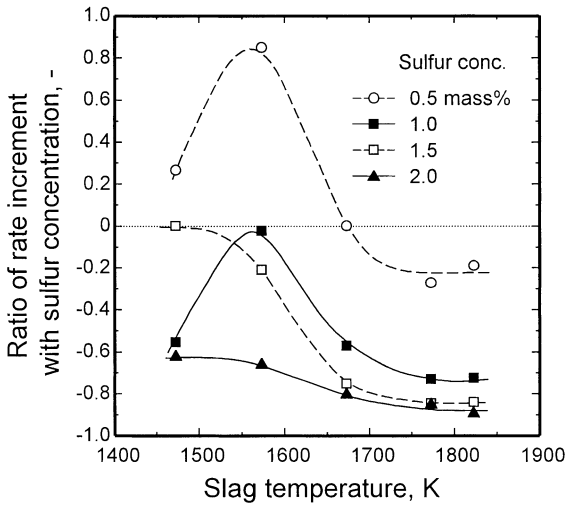


Fig. 8. Plots of ratio of rate increment with sulfur concentration against slag temperature.

slag temperature.

$$r_s = \frac{R_i^{*S} - R_0^{*S}}{R_0^{*S}} \dots\dots\dots(7)$$

where,  $R_i^{*S}$  and  $R_0^{*S}$  are the rates of methane–steam reaction for the sulfur concentrations of  $i$  and 0 mass% at a given temperature, respectively. For the sulfur concentrations higher than 1.0 mass%,  $r_s$  is negative in the whole slag temperature range examined, apparently meaning the inhibitory effect of sulfur on the methane–steam reaction. For the slags containing 1.0 and 1.5 mass% S, drastic decrease in  $r_s$  takes place against the temperature increase from 1 573 to 1 673 K, and then slight decrease in  $r_s$  follows with further increase of the temperature. For the sulfur concentration of 2.0 mass%,  $r_s$  decreases moderately from around  $-0.6$  to  $-0.9$  with increasing the slag temperature from 1 473 to 1 823 K. For all the slags,  $r_s$  is independent on the slag temperature above 1 773 K. In contrast, it depends strongly on the sulfur concentration from 0.5 to 1.0 mass%, and insignificantly on that more than 1.0 mass%. This result re-

veals that the inhibitory effect of sulfur appears considerably for the slag containing about 1.0 mass% S. Moreover, the further sulfur contamination to slag brings about the insignificant enhancement of the inhibitory effect.

As mentioned above, both of FeO and sulfur have inhibitory effect on the methane–steam reaction. However, the mechanism might be different from each other because the iron exists in molten slag in a form of cation, whereas the sulfur does in that of anion.<sup>9)</sup> As suggested above, the calcium in molten slag, which is present as cation, has a possibility to become a site for the methane–steam reaction. Thus, from the experimental results, the sulfur anion is suggested to work on the calcium cation to negate its role as the reaction site.

4. Conclusions

Rate of the methane–steam reaction on slag surface was studied for thirteen slag samples having different compositions. In this study, effects of mass ratio of CaO to SiO<sub>2</sub> (CaO/SiO<sub>2</sub> ratio) in slag, and FeO and sulfur concentrations in slag on the reaction rate, were systematically examined in the slag temperature range from 1 473 to 1 823 K. The results are summarized as follows:

- (1) Increase in CaO/SiO<sub>2</sub> ratio, which provides the reduction in strength of network structure of molten slag, gives rise to increase in the rate of methane–steam reaction.
- (2) FeO addition to slag has an inhibitory effect on the methane–steam reaction, which inhibits the reaction more strongly in proportion to the FeO concentration above the slag temperature of 1 773 K.
- (3) The methane–steam reaction is suppressed considerably by the sulfur contained in slag, depending on the sulfur concentration from 0.5 to 1.0 mass%. Further increase in the sulfur concentration affects insignificantly the inhibitory effect.

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