Note

Generation Behavior of H$_2$ Gas by Reaction between FeO-containing Slag and H$_2$O–Ar Gas

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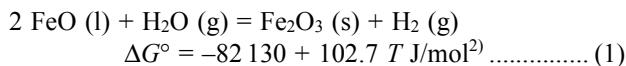
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1. Introduction

Steelmaking slag which is generated from steelmaking process with converters is a main by-product of steel and discharged at temperature range between 1 873 and 1 923 K after discharging of refined molten steel. Amount of generated steelmaking slag is 11.7 Mt/y (FY2010) in Japan,[1] and thus the enormous heat is released from steelmaking process by steelmaking slag. Steelmaking slag contains large concentration of FeO from 20 to 30 mass%, and reduction of H$_2$O gas by FeO contained in steelmaking slag is expected as reaction (1),

$$2\ FeO\ (l) + H_2O\ (g) = Fe_2O_3\ (s) + H_2\ (g)$$
$$\Delta G° = -82\,130 + 102.7\ T\ \text{J/mol}^{[2]} \ \ldots\ldots (1)$$

Although this reaction does not proceed forward spontaneously in standards states of reactants and products, progress of the reaction to equilibrium is expected. Furthermore, because of the exothermic reaction, no heat or only small heat supply may be required to maintain reaction system at steady state. From above considerations, environmental-friendly H$_2$ gas production process could be developed by utilizing slag and heat generated by converter process.

In the previous study,[3] thermodynamics of the reaction between steelmaking slag and H$_2$O-containing gas was studied by thermodynamic calculation and effects of compositions and temperature of slag and gas were clarified. Based on the thermodynamic estimations, generation of H$_2$ gas is expected to some extent.

In the present study, generation behavior of H$_2$ gas by reaction between FeO-containing slag and H$_2$O–Ar gas was measured at 1 723 K and the effect of slag compositions was studied.

2. Experimental

The weight change of the FeO–CaO–SiO$_2$–Al$_2$O$_3$–MgO–P$_2$O$_5$ slag was measured after reaction with gas to measure generation behavior of H$_2$ gas by reaction between FeO-

containing slag and H$_2$O-containing gas. Slag samples were prepared by following procedures. FeO was prepared by melting equimolar mixture of reagent grade Fe powder and Fe$_2$O$_3$ or Fe$_3$O$_4$ powder in an iron crucible at 1 723 K for 1 h at Ar atmosphere and quenching the melt on a steel plate with blowing Ar gas. CaO was prepared by calcining reagent grade CaCO$_3$ in a mullite Tammann tube at 1 273 K for 12 h. Prepared FeO and CaO, and reagent grade SiO$_2$, Al$_2$O$_3$, MgO and Ca$_3$(PO$_4$)$_2$ were mixed with prescribed ratios and the mixture was melted in an iron crucible at 1 723 K for 1 h at Ar atmosphere. The premelted slag was quenched on a steel plate with blowing Ar gas.

Figure 1 shows the schematic diagram of the experimental apparatus, which consists of a gas circuit for preparation of H$_2$O–Ar gas with constant H$_2$O partial pressure and an electric furnace with a mullite reaction tube (O.D. 50 mm, I.D. 42 mm, length 1 000 mm). Three Erlenmeyer flasks with distilled water were connected in series and put inside a thermostat bath kept at 333 K. Argon gas was continuously supplied into flasks with flow rate of 300 cm^3/min and 0.2 atm H$_2$O–Ar gas was obtained. Further Ar gas was mixed with flow rate of 500 cm^3/min to increase the gas flow rate and finally 0.086 atm H$_2$O–Ar gas was blown to the surface of molten slags through a mullite tube (O.D. 6 mm, I.D. 4 mm) which tip was kept at the position of 25 mm above the slag surface. A Pt crucible (upper diameter 36 mm, bottom diameter 22 mm, height 40 mm, volume 30 cm^3) was employed to keep 10 g of molten slag at Ar atmosphere. After the slag sample was melted completely, H$_2$O–Ar gas was introduced onto the sample. Count of reaction time started when the gas was switched. After prescribed reaction time passed, H$_2$O–Ar gas was changed to Ar gas and the reaction tube was purged, and then the Pt crucible was quickly taken out of the reaction tube and quenched by blowing Ar gas. The whole sample after quenching was taken out of the Pt crucible and pulverized to be analyzed.

Weights of samples with the Pt crucible before and after each experiment were measured, and chemical compositions of slags before and after experimens were analyzed by following methods, total Fe and Fe^{2+} contents by titration method with potassium dichromate, SiO$_2$ by gravimetry, Al and Mg by ICP–OES of acid solution, and P by molybdenum blue spectrophotometric method.
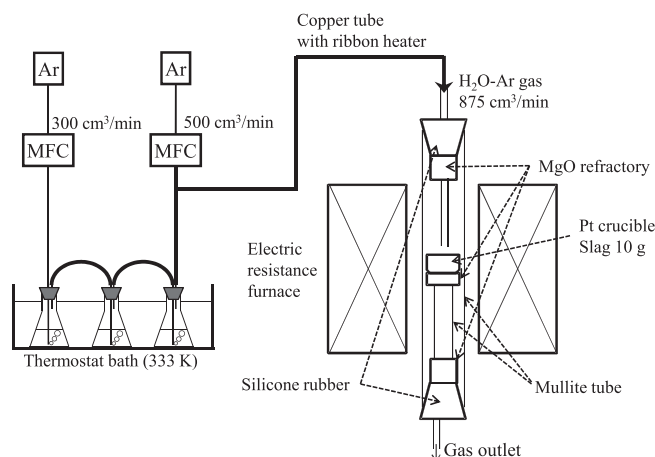

Fig. 1. Schematic diagram of experimental apparatus.

3. Results and Discussion

Table 1 shows the experimental conditions and results. In the present experiments, 0.086 atm H_2O–Ar gas with flow rate of 875 cm^3/min and 10 g of molten slag were reacted for 15 to 120 min at 1 723 K. Four kinds of slags were prepared with various FeO contents and mass%CaO/mass%SiO_2 ratios, while Al_2O_3, MgO and P_2O_5 contents were almost maintained constant. After all experiments, the weights of slags increased. Chemical compositions of synthesized slags and samples after reaction are shown in **Table 2**.

Figure 2 shows the relationship between weight increase and reaction time for four slag samples. Weights of all slags increased monotonously with time. The increment at the initial 15 min was the largest and similar for all slags. On the contrary, the increasing rates of slag weights after 15 min were different between slags, which is due to the difference in FeO content of slags. When all FeO in slags are oxidized to Fe_2O_3, the estimated increase in slag weights are 0.520, 0.538, 0.406 and 0.312 g for slags A, B, C and D, respectively, and the reaction ratios, defined as the ratios of increase in observed weights to its estimated ones, are 43.0, 50.5, 32.2 and 32.2% for slags A, B, C and D, respectively. The reaction ratio increased with increasing initial FeO content in slag. This difference would be due to change of conditions of molten slag surface, such as partial solidification of slag surface because of the oxidation of FeO to Fe_2O_3.

As shown in Table 2, FeO and Fe_2O_3 contents decreased and increased respectively while contents of other oxides did not change clearly, which means FeO was oxidized to Fe_2O_3. **Figure 3** shows the change in FeO content of slags with reaction time. FeO contents of all slags decreased monotonously with time. Comparing slags A and B, FeO content of slag B decreased more than that of slag A. Initial

FeO contents of these slags were almost the same, however mass ratio of CaO to SiO_2 for slag B was larger than that for slag A. Activity of FeO in slags estimated for the FeO–CaO–SiO_2 system[4] at 1 723 K are 0.56 and 0.63 for slags A and B, respectively. Considering reaction (1), larger FeO activity increases the forward reaction rate more. Therefore, FeO in slag B is oxidized more than that in slag A.

In the present experiments, compositions of exhaust gas were not analyzed and thus the generation of H_2 gas was not

Table 2. Chemical compositions of slags before and after experiments.

(Unit: mass%)

	FeO	Fe_2O_3	CaO	SiO_2	Al_2O_3	MgO	P_2O_5	Total
Slag								
A	46.66	3.41	18.48	22.9	1.86	5.62	0.86	99.8
B	48.36	2.53	20.88	16.3	1.93	5.43	0.82	96.2
C	36.47	6.74	22.80	24.7	1.83	5.40	1.50	99.1
D	27.98	5.53	24.97	30.7	1.74	5.00	0.88	96.8
Exp. No.								
1	36.84	15.38	18.04	20.2	1.67	5.29	0.88	98.3
2	34.61	18.33	18.28	18.4	1.81	5.36	0.89	97.6
3	35.30	17.74	18.16	21.8	1.73	5.23	0.88	100.8
4	31.91	19.49	18.14	18.6	1.72	5.23	0.87	96.0
5	31.24	21.91	18.12	19.2	1.81	5.15	0.88	98.3
6	35.63	18.26	20.09	14.3	1.71	5.24	0.89	96.2
7	33.98	21.69	20.32	17.4	1.82	5.32	0.88	101.4
8	31.26	23.64	20.03	16.8	1.69	5.20	0.88	99.5
9	26.09	28.63	20.62	14.3	1.76	5.27	0.90	97.6
10	29.72	12.07	22.45	23.8	1.87	5.26	1.50	96.6
11	28.25	13.79	22.33	23.9	1.90	5.29	1.50	96.8
12	27.14	15.18	22.15	24.9	1.80	5.18	1.50	97.6
13	23.89	17.83	22.01	23.0	1.84	5.19	1.50	95.1
14	23.88	9.40	25.86	26.0	1.83	5.15	0.86	93.0
15	23.26	8.43	25.53	28.8	1.83	5.14	0.89	93.9
16	20.59	11.81	24.67	26.1	1.73	4.92	0.84	90.7
17	19.56	14.98	24.93	28.6	1.83	5.03	0.84	95.8

Table 1. Experimental conditions and results.

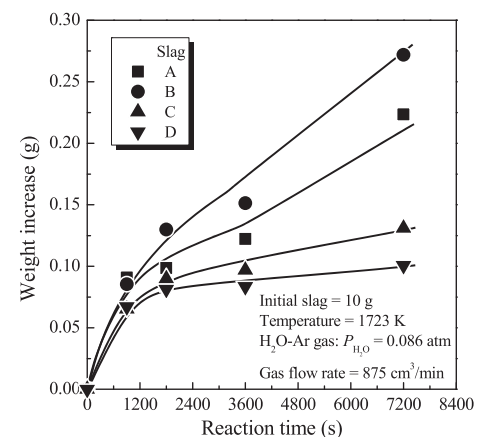| Exp. No.	Slag	Temp.	Gas	Reaction time (min)	Weight increase (g)
1	A			15	0.0908
2	A			30	0.0845
3	A			30	0.0986
4	A			60	0.1222
5	A			120	0.2235
6	B			15	0.0854
7	B			30	0.1298
8	B			60	0.1513
9	B	1 723 K	H_2O–Ar $P(H_2O) = 0.086$ atm 875 cm^3/min	120	0.2719
10	C			15	0.0652
11	C			30	0.0898
12	C			60	0.0969
13	C			120	0.1309
14	D			15	0.0671
15	D			30	0.0812
16	D			60	0.0835
17	D			120	0.1006

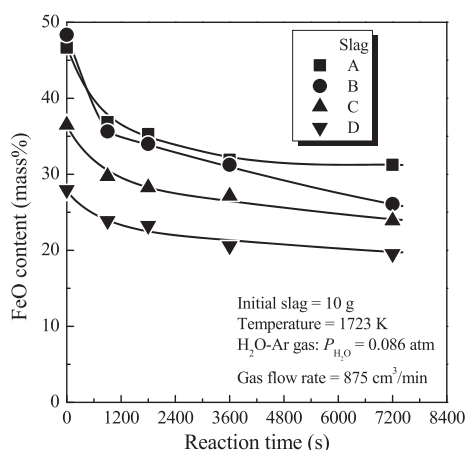**Fig. 2.** Relationship between weight increase and reaction time.

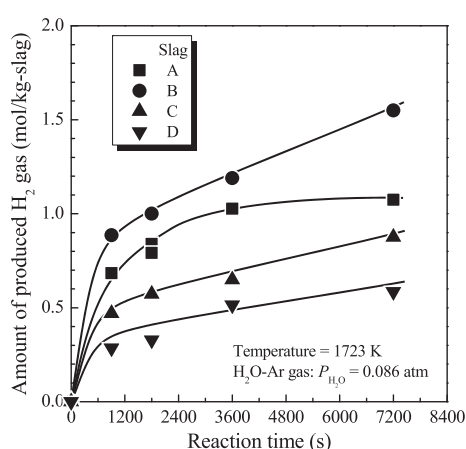**Fig. 3.** Change in FeO content of slags with reaction time.

Fig. 4. Relationship between calculated amount of produced H_2 gas and reaction time.

directly confirmed. However, H_2 gas was probably generated by reaction between FeO in slag and H_2O gas from above results and discussion. Number of moles of generated H_2 gas was estimated from change of FeO composition with the following equation:

$$N_{H_2} = \frac{-\Delta C_{FeO}}{100} \times W_{slag} \times \frac{1}{71.85} \times \frac{1}{2} \quad \text{............. (2)}$$

where N_{H_2} is the amount of generated H_2 gas (mol), ΔC_{FeO} is the change in FeO content (mass%) of slag and W_{slag} is initial weight (g) of slag. **Figure 4** shows the relationship between estimated amount of produced H_2 gas per 1 kg of slag and reaction time. Amount of generated H_2 gas increased with increasing initial FeO content and time,

although the generation rate of H_2 gas decreased with time, which is consistent to results of thermodynamic calculation for reaction between the FeO–CaO–SiO_2 slag and H_2O–Ar gas in our previous study.[3] Since this study was conducted in a flow system, the measured generation rates of H_2 gas are the maximal ones at the present experimental conditions.

Present experiments were conducted for slags with mass ratio of CaO to SiO_2 from 0.80 to 1.28 and temperature at 1 723 K because of the regulation of experimental setup and thus the direct estimation regarding H_2 gas generation behavior from converter steelmaking slag is difficult. However, for instance, in the case of slag D which initial FeO content was 28 mass%, 0.59 mol-H_2/kg-slag were generated after reaction with 0.086 atm H_2O–Ar gas for 120 min. Assuming that amount of converter slag generated with 300 t capacity converter is 30 t and 0.59 mol-H_2/kg-slag is generated by slag–gas reaction, 17 700 mol or 396 m^3 STP H_2 gas would be produced from this slag. Considering that practical converter slag contains fine steel particles, the amount of produced H_2 gas is expected to increase further. In this study, the generation rate of H_2 gas was measured at constant temperature. However, when we develop the environmental-friendly H_2 production process with converter slag and H_2O gas, process conditions such as temperature drop, reaction rate between slag and gas or generation of various solid phases from slag with progress of oxidation reaction must be deeply considered.

4. Conclusions

Generation behavior of H_2 gas by reaction between FeO-containing slag and H_2O–Ar gas was measured at 1 723 K with four kinds of synthesized FeO–CaO–SiO_2–Al_2O_3–MgO–P_2O_5 slag. From 32.2 to 50.5% of FeO contained in slags were oxidized to Fe_2O_3 by 0.086 atm H_2O–Ar gas for 120 min. Maximal amount of generated H_2 gas estimated from composition change was 0.59 mol-H_2/kg-slag for 120 min at present experimental conditions.

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4) Verein Deutscher Eisenhüttenleute, ed.: SLAG ATLAS, 2nd ed., Verlag Stahleisen GmbH, D-Düsseldorf, (1995), 243.