Thermodynamic Calculation of Generation of H₂ Gas by Reaction between FeO in Steelmaking Slag and Water Vapor

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Hydrogen gas is one of key materials for promotion of the utilization of energy with low environmental load. Ironmaking and steelmaking processes produce enormous thermal energy during steel production, most of which are not used before final dissipation to natural environment. In the present study, the environmental-friendly H₂ gas production process by converting H₂O gas with FeO and thermal energy in steelmaking slag has been proposed, and physicochemical properties of reaction between FeO-containing steelmaking slag and H₂O-containing gas have been estimated by applying thermodynamic calculation. The effects of slag temperature and compositions, gas temperature, and partial pressure of H₂O on production behavior of H₂ gas have been investigated.

KEY WORDS: physical chemistry; hydrogen gas; steelmaking slag; FeO; steam; energy conversion.

1. Introduction

Ironmaking and steelmaking processes via blast furnace – converter process from iron ore are an essential steel production route for Japanese steel industries to stably supply high quality steel products in large quantity to society. Blast furnace – converter process consumes huge amount of fossil fuels such as mainly coal, resulting the emission of considerable amount of CO₂ gas. Since the emission of CO₂ gas from steel industries accounts for approximately 12% of domestic CO₂ gas emission in Japan (FY2009), it is an urgent issue to develop environmental-friendly ironmaking and steelmaking processes and reduce CO₂ emission for steel industries.

Various kinds of gases and by-products generated from ironmaking and steelmaking processes are recycled as much as possible at present. Enormous thermal energy is also generated from processes and released to surrounding atmosphere as various forms such as sensible heats of gases, molten steels or by-products, and as heat losses. However, these energies are not utilized before final dissipation to atmosphere. Although various technologies to utilize thermal energy from ironmaking and steelmaking processes have been attempted to develop, practical application of these technologies has not been achieved because the thermal energy is not always useful as an energy source.

In steelmaking process by converter, fluxing agent such as CaO is added during reheating and about 100 kg/t-steel of steelmaking slag are generated. Since the steelmaking slag is discharged at temperature range between 1 873 and 1 923 K after discharge of refined molten steel, it has large thermal energy. Amount of generated steelmaking slag is 11.7 Mt/y (FY2010) in Japan. Assuming the amount of steelmaking slag is 10 Mt/y and its heat capacity from room temperature to 1 923 K is 1 J/g·K estimated from the value for the Al₂O₃–CaO–FeOₓ–MgO–MnO–P₂O₅–SiO₂ system, unutilized heat is estimated to be 16 PJ, which is equal to annual energy consumption of 420 thousand families in Japan. Since steelmaking slag contains relatively large concentration of FeO in the range from 20 to 30 mass%, reduction of H₂O gas by FeO described as reaction (1) is expected,

\[
2 \text{FeO (l)} + \text{H}_2\text{O (g)} = \text{Fe}_2\text{O}_3 (s) + \text{H}_2 (g)
\]

\[\Delta G^\circ = -82 130 + 102.7 T \text{ J/mol}^0 \]

From Gibbs free energy change of reaction (1), this reaction does not proceed forward spontaneously in standards states of reactants and products, and progress of the reaction to equilibrium is expected. In addition, no heat or only small heat supply may be necessary because reaction (1) is exothermic, and thus it is considered that thermal energy required for stable operation could be supplied sufficiently by sensible heat of converter slag. From above reasons, the development of energy-saving H₂ production process without further energy consumption would be possible.

However, FeO and Fe₂O₃ contents in the slag decrease and increase, respectively, with progress of reaction (1). This compositional change results in the increment in solid fraction or viscosity of slag affecting the physical properties of slag such as fluidity and thus operational condition of H₂ gas production process. Accordingly, sufficient understanding of the physical chemistry of reaction between slag containing FeO and steam gas is important for precise operation of the process.

In the present study, thermodynamics of the reaction between the FeO–CaO–SiO₂ slag system and H₂O–Ar gas...
was studied by thermodynamic calculation and the effects of temperatures, compositions of gas and slag on the behavior of \( \text{H}_2 \) gas production or the physicochemical properties of slag were clarified.

2. Conditions for Thermodynamic Calculation

In the present study, thermodynamic calculation software FactSage 6.2 was used for estimation of equilibrium state between FeO-containing slag and H2O-containing gas, and \( \text{H}_2 \) gas generation behavior.

Table 1 shows the detail of calculation conditions. Firstly, the initial condensed phases including molten slag and solid oxides were prepared by inputting oxide constituents with prescribed compositions and equilibrating at initial slag temperature. Subsequently the prepared condensed phases were equilibrated with H2O–Ar gas. In the case of the preparation of initial condensed phases, FeO, CaO and SiO2 were input to be 1 kg as a total, and then 56 kinds of pure compounds (pure liquid species: 7 and pure solid species: 49) and 12 kinds of solutions considering 39 species were considered in the equilibrium calculation as final candidates at predetermined temperature. In this stage, the formation of gas phase was not allowed. Non molten slag phases such as metallic or 2CaO·SiO2 phase were formed in some calculations and these phases were also taken into account for slag-gas equilibrium calculation. In the slag-gas equilibrium calculation, 105 kinds of pure compounds (pure gaseous species in ideal behavior: 26, pure liquid species: 9 and pure solid species: 70) and 12 kinds of solutions considering 40 species were considered in the equilibrium calculation as final candidates. For the estimation of change in composition of condensed phases and system temperature with proceeding of reaction between slag and gas, 10 L of H2O–Ar gas at predetermined gas temperature were equilibrated with condensed phases at the condition of no enthalpy change of the system at one calculation step. Condensed phases such as molten slag or various solids after equilibrium calculation were input as initial condensed phases in the next calculation, and 10 L of new H2O–Ar gas were equilibrated again. The above equilibrium calculation between slag and gas was repeated by decreasing temperature less than 1722 K. Change in slag compositions and system temperature with process of reaction between slag and gas were estimated.

3. Results and Discussion

3.1. Effect of Gas Temperature and Slag Composition

To clarify the effect of gas temperature and initial slag composition, gas temperature and initial FeO content of slag were varied in the ranges between 473 and 1273 K, and between 10 and 40 mass%, respectively, with 2 or 3 of...
mass%CaO/mass%SiO2 ratio, maintaining initial slag temperature and partial pressure of H2O in H2O–Ar gas as 1873 K and 1.0 atm (no Ar gas), respectively.

**Figures 1 and 2** show the change in the amount of produced H2 gas with volume of introduced H2O gas. The amount of produced H2 gas is here the accumulated amount of H2 gas produced by repetitive slag-gas equilibrium calculation. Increase in introduced gas temperature increased the amount of produced H2 gas in all calculation conditions, which is because temperature drop by equilibrium between gas and slag became smaller with increasing gas temperature and thus more H2O gas reacted with FeO contained in slag. Increase in initial FeO content in slag and mass%CaO/mass%SiO2 ratio increased the amount of produced H2 gas.

**Figures 3 and 4** show the change in solid fraction of slag phase with introduced gas volume. With larger mass%CaO/mass%SiO2 ratio, the solid fraction of slag phase is larger, FeO content in liquid phase increases and thus the amount of reacted H2O increases. As shown in Fig. 3(d), the calculated solid fractions are very small as almost 0 when mass%CaO/mass%SiO2 ratio is 2 and FeO content is 40 mass%. Therefore, increase in solid fraction of slag phase is favorable from the viewpoint of FeO condensation in liquid phase resulting the increase in the amount of H2 gas production, while fluidity of slag also becomes worse with increasing solid fraction, which various disadvantageous conditions are induced. Accordingly, the best conditions in solid fraction characterizing slag fluidity and reactivity with H2O gas must be clarified.

**Figures 5 and 6** show the change in production ratio of H2 gas with introduced H2O gas volume, where production ratio of H2 gas is defined as the molar ratio of the amount of generated H2 gas to that of introduced 10 L H2O–Ar gas in one equilibrium calculation. The effect of gas temperature or slag composition on the production ratio of H2 gas is small. The production ratio of H2 gas is the largest at the beginning of reaction, from 60 to 85%, and decreases much with increasing introduced gas volume.

**Figures 7 and 8** show the change in slag temperature with introduced gas volume. Although reaction (1) is exothermic, system temperature decreases with increasing introduced gas volume because temperature of the introduced gas is lower than that of slag and thus thermal energies of slag and generated heat by reaction (1) are flown out as sensible heat of exhaust gas. In the case of mass%CaO/mass%SiO2 ratio of 2, slag temperature decreases monotonically with increasing introduced gas volume as shown in Fig. 7. On the contrary, as shown in Fig. 8, slag temperature increases once after decreases at the initial stage, and then decreases again with increasing introduced gas volume. This transient temperature increase is due to the increase of solid fraction as shown in Fig. 4, because FeO in slag is oxidized by H2O gas to Fe2O3 and liquidus temperature changes. In the present calculation conditions, temperature increases transiently because solid fraction drastically increases during slag-gas reaction and heat is generated more than that required for compensation of slag temperature decrease. However, the drastic increase in the amount of produced H2 gas due to drastic increase of slag temperature is not observed as shown in Fig. 2.
Fig. 2. Change in produced amount of H₂ gas with introduced gas volume; initial slag temperature = 1873 K, mass%CaO/mass%SiO₂ ratio = 3, P(H₂O) = 1 atm, initial FeO content: (a) 10 mass%, (b) 20 mass%, (c) 30 mass%, and (d) 40 mass%.

Fig. 3. Change in fraction of solid phase in slag with introduced gas volume; initial slag temperature = 1873 K, mass%CaO/mass%SiO₂ ratio = 2, P(H₂O) = 1 atm, initial FeO content: (a) 10 mass%, (b) 20 mass%, (c) 30 mass%, and (d) 40 mass%.
Fig. 4. Change in fraction of solid phase in slag with introduced gas volume; initial slag temperature = 1 873 K, mass%CaO/mass%SiO₂ ratio = 3, \( P(H_2O) \) = 1 atm, initial FeO content: (a) 10 mass\%, (b) 20 mass\%, (c) 30 mass\%, and (d) 40 mass\%.

Fig. 5. Change in production ratio of H₂ gas with introduced gas volume; initial slag temperature = 1 873 K, mass%CaO/mass%SiO₂ ratio = 2, \( P(H_2O) \) = 1 atm, initial FeO content: (a) 10 mass\%, (b) 20 mass\%, (c) 30 mass\%, and (d) 40 mass\%.
Fig. 6. Change in production ratio of H$_2$ gas with introduced gas volume; initial slag temperature = 1873 K, mass%CaO/mass%SiO$_2$ ratio = 3, $P$(H$_2$O) = 1 atm, initial FeO content: (a) 10 mass%, (b) 20 mass%, (c) 30 mass%, and (d) 40 mass%.

Fig. 7. Change in slag temperature with introduced gas volume; initial slag temperature = 1873 K, mass%CaO/mass%SiO$_2$ ratio = 2, $P$(H$_2$O) = 1 atm, initial FeO content: (a) 10 mass%, (b) 20 mass%, (c) 30 mass%, and (d) 40 mass%.
3.2. Effect of Initial Slag Temperature

The effect of initial slag temperature on the production behavior of H₂ gas was studied by varying initial slag temperature in the range between 1 873 and 1 973 K with 20 or 40 mass% of initial FeO content, maintaining initial slag mass%CaO/mass%SiO₂ ratio as 2, gas temperature as 1 273 K and partial pressure of H₂O in H₂O–Ar gas as 1.0 atm (no Ar gas), respectively.

Figures 9 and 10 show the change in the amount of produced H₂ gas and production ratio of H₂ gas with introduced H₂O gas volume, respectively. The effect of initial slag temperature on these relationships is quite small but the end of slag-gas reaction (temperature reaches 1 772 K) is different with different initial slag temperature. Total amount of produced H₂ gas increases with higher initial slag temperature because more H₂O gas is possible to react with slag before temperature reaches 1 772 K. However, the production ratio of H₂ gas decreases with increasing introduced H₂O gas volume as shown in Fig. 10, and the production efficiency decreases.

Figures 11 and 12 show the change in solid fraction and slag temperature with introduced H₂O gas volume, respectively. Solid phases are formed in the case of 20 mass%FeO, while no solid phase appears in the case of 40 mass%FeO. The relationship between solid fraction and introduced gas volume varies with different initial slag temperature. How-
ever, those change rate is almost the same. The similar behavior is observed in the case of slag temperature change. The folding points are seen in Fig. 12, which correspond to initiation points of the formation of solid phases.

3.3. Effect of Partial Pressure of H2O in H2O–Ar Gas

The effect of H2O partial pressure in introduced H2O–Ar gas on the production of H2 gas was calculated in H2O partial pressure from 0.1 to 1.0 atm in H2O–Ar gas. Introduced H2O–Ar gas temperature, initial slag temperature, and initial slag composition were fixed as 1 273 K, 1 933 K, mass%CaO/mass%SiO2 ratio as 2 and 20 mass%FeO, respectively.

Figures 13 to 16 show the change in produced amount of H2 gas, production ratio of H2 gas, solid fraction and slag temperature with introduced gas volume, respectively. The amount increases with increasing partial pressure of H2O in the initial gas, while production ratio of H2 decreases. Since...
more amount of FeO is oxidized to Fe₂O₃ by gas with larger H₂O partial pressure, solid fraction is larger. Although H₂ gas is produced more and solid fraction is larger with increasing H₂O partial pressure, slag temperature decreases more steeply. This is because of the large difference in heat capacities of Ar (20.786 J/mol·K at 300 to 1300 K⁶) and H₂O (from 33.596 to 44.945 J/mol·K at 300 to 1300 K⁷) gases.

Figure 17 shows the relationship between total amount or total production ratio of H₂ gas and partial pressure of H₂O in introduced gas.
production ratio of $H_2$ gas and partial pressure of $H_2O$ in introduced $H_2O$–$Ar$ gas. The amount of produced $H_2$ gas increased with increasing $H_2O$ partial pressure, while the production ratio decreased. Figure 18 shows the relationship between partial pressure of $H_2$ in totally produced $H_2$–$H_2O$–$Ar$ gas and that of $H_2O$ in introduced $H_2O$–$Ar$ gas. In this calculation condition, $H_2$ partial pressure increases with increasing $H_2O$ partial pressure which indicates $H_2$ could be easily concentrated when pure $H_2O$ gas is reacted with slag. However, the most suitable $H_2O$ partial pressure may be different in other conditions and thus it should be predicted based on the considered conditions such as slag temperature and compositions, or gas temperature.

4. Conclusions

In the present study, the environmental-friendly $H_2$ production process utilizing FeO and thermal energy in steel-making slag has been proposed and thermodynamics of reaction between steelmaking slag and $H_2O$–$Ar$ gas has been studied by applying thermodynamic calculation. The obtained results are summarized as follows.

(1) FeO in slag and $H_2O$ gas reacts to equilibrium and $H_2$ gas is produced.
(2) Increase in gas temperature and FeO content in slag increase produced amount of $H_2$ gas. Progression of FeO oxidation to $Fe_2O_3$ increases the solid fraction of slag which will lead the deterioration of slag fluidity while FeO is concentrated in liquid phase and reactivity with $H_2O$ gas is improved.
(3) Initial slag temperature does not influence the relationship between produced amount or production ratio of $H_2$ gas and introduced gas volume, but affects the end point of slag-gas reaction.
(4) Increase in partial pressure of $H_2O$ in introduced $H_2O$–$Ar$ gas increases the produced amount of $H_2$ gas, while the production ratio decreases. Steeper temperature drop despite larger heat evolution by reaction and solid phase formation is due to large difference in heat capacities of $Ar$ and $H_2O$ gases. The best condition to reach optimal production amount and large concentration of $H_2$ gas depends on slag temperature and compositions, gas temperature and $H_2O$ partial pressure.

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