1. Introduction

In the Kyoto protocol, Japanese government engaged that our country would reduce 6% of greenhouse gas emissions from 1990 levels by the year 2012. CO$_2$ emissions in the steel industry make up for about 15% of total emissions in Japan.\(^1\) Especially, CO$_2$ emissions in ironmaking process account for about 70% in the steel industry. Therefore, reduction of CO$_2$ gas from the ironmaking process is a pressing issue to avoid global warming.

One of the promising solutions is an effective use of organic waste materials including waste plastic materials in the ironmaking process. Waste plastic materials contain a huge amount of hydrogen. The hydrogen is advantageous rather than CO gas to the reduction of iron oxide. Besides, utilization of waste plastic materials enables the process to reduce CO$_2$ emissions due to substitution of the plastic materials for the conventional fossil fuels. Based on this background, researches on utilization of waste plastic materials in the ironmaking process have been actively conducted in recent years. Some results of the researches\(^2\)–\(^4\) have already been applied to actual processes, for examples, a partial alternative of coal by waste plastics at coke ovens and injections of waste plastics into blast furnaces.

On the other hand, carbon composite method,\(^5\)–\(^10\) which uses a briquetted mixture of iron ores and coals, enhances the reaction rate considerably, and the method is also expected to reduce CO$_2$ emissions in the ironmaking process. Therefore, utilization of waste plastic materials as reducing agent in the carbon composite method is expected to contribute to deterrence of global warming. This technology is also expected to help both suppression of CO$_2$ emissions and recovery of H$_2$ and CO gases from waste plastic materials. However, there are few researches\(^11\)–\(^14\) on this technology which utilize waste plastic materials as reducing agent in the carbon composite method.

By the way, about 40% of volume of household garbage is waste plastics,\(^15\) and major component of the waste plastics is polyethylene (–CH$_2$–CH$_2$–)\(_n\) (hereafter PE). Moreover, Refuse Derived Fuel (hereafter RDF) is mainly made from waste plastics. Therefore, PE and RDF were used as typical waste plastic materials in this experiment.

In this study, we investigated the thermal decomposition behavior of PE and RDF and the reaction behavior of PE/RDF and iron oxide mixtures.

2. Experiment

2.1. Experimental Samples

The particle diameters of PE reagent powders were ~425 µm. RDF was crushed and screened to obtain samples having ~60 µm in diameter. Table 1 shows properties of the PE reagent and RDF powders. PE consists entirely of hydrogen and carbon. On the other hand, RDF includes oxygen, fixed carbon and ash.

In thermal decomposition experiments, 0.39 g of PE...
powders was directly used as experimental samples. 1.5 g of RDF powders was pressed into 7 mm height tablet shape using a die of 15 mm in inner diameter.

In reduction experiments, weighed PE or RDF powders and hematite reagent powders were mixed as shown in Table 2. Molar ratios of carbon to oxygen, hydrogen to oxygen, and carbon and hydrogen to oxygen in the samples are also shown in the same table. H-PE sample was pressed into 7 mm height tablet shape using the die. H-RDF sample was also pressed into 15 mm height tablet shape using the same die.

2.2. Experimental Method

Figure 1 shows a schematic diagram of the experimental apparatus. The reaction tube was vertical type alumina tube of 35 mm in the inner diameter.

The sample was placed in a Pt basket, and the basket was suspended by a Pt wire connecting with the thermo balance. The electric resistance furnace was maintained at experimental temperatures of 1 000, 1 100, 1 200 and 1 300°C. When the furnace reached the experimental temperatures, the basket was inserted into isothermal zone. This timing was defined as heating start time in this experiment. The Ar gas was introduced at a flow rate of 3.33 ×10⁻³ m³/s to the reaction tube as a carried gas.

The generated gases from samples were introduced into the quad-pole mass spectrometer via the filter and cold trap (−10°C). Fine particles such as soot, tar and water in generated gases were removed by the filter and the cold trap, respectively. 

H₂, CO, CO₂, CH₄, C₂H₂ and C₂H₄ concentrations of generated gases were measured continuously by the quad-pole mass spectrometer. H₂O concentration of generated gas and weight changes of the samples were measured continuously by the humidity meter and the thermo balance, respectively. When the weight changes of the samples reached stagnant period, the samples were rapidly cooled in the Ar gas stream. After reduction experiments, total Fe, metallic Fe and Fe²⁺ in samples were analyzed by chemical analysis to determine the fractional reduction of samples.

2.3. Definition of Conversion Ratio

This study adopted a conversion ratio to evaluate recovery amount of gases from the waste plastic materials. A value of the conversion ratio shows how much hydrogen and carbon were decomposed into utilizable gases from waste plastic materials during the thermal decomposition and the reduction reaction.

\[
CR_H = H_G / H_{Waste} \times 100..........................(1)
\]

\[
CR_C = C_G / C_{Waste} \times 100..........................(2)
\]

Where, \(CR_H(\%)\) and \(CR_C(\%)\) are the conversion ratios of hydrogen and carbon, respectively. \(H_G(\text{mol})\) and \(C_G(\text{mol})\) are the number of moles of hydrogen atom and carbon atom in the recovered gases, respectively. \(H_{Waste}(\text{mol})\) and \(C_{Waste}(\text{mol})\) are the number of moles of hydrogen atom and carbon atom in the initial waste plastic materials, respectively.

3. Results and Discussions

3.1. Thermal Decomposition of PE and RDF

Figure 2 shows gas generation behavior in the thermal decomposition experiment of PE sample at 1 000°C. In the case of PE sample, flow rates of each generated gas reached the maximum values in about 30 s, and gas generation finished in about 100 s. The reason is that ISIJ International, Vol. 48 (2008), No. 12
the RDF contains thermally persistent components such as small pieces of paper. The volume of generated H$_2$ was the largest in the detected gases. CO, CO$_2$ and H$_2$O were detected because RDF contains oxygen itself differ from PE. After experiment, residual carbon existed as not only adhesion soot at the reaction tube and the filter but also char in the Pt basket.

Gas generation behaviors in the thermal decomposition experiments of PE and RDF samples at 1200°C are shown in Figs. 4 and 5, respectively. The thermal decomposition of the samples finished in a shorter period of time by increasing temperature. Furthermore, volume of H$_2$ increased in both samples, and the volume of CO increased in RDF sample by increasing temperature from 1000 to 1200°C.

3.2. Reduction of PE/RDF and Iron Oxide Mixtures

Gas generation behavior in the reduction experiment of H-PE sample at 1000°C are shown in Fig. 6. The final fractional reduction of H-PE sample at 1000°C was 40%. In the case of H-PE sample, major component of generated gases were H$_2$ and CH$_4$ as same as in the case of PE sample shown in Fig. 2. The occurrence of iron oxide reduction by H$_2$ was confirmed by a detection of H$_2$O. Flow rates of generated gases became the maximum values in around 30–60 s except CO. CO was not detected in the first period of the reaction, and CO was detected in the middle and last periods in about 90–240 s. The flow rate of CO became the maximum value in about 160 s.

Gas generation behavior in the reduction experiment of H-RDF sample at 1000°C are shown in Fig. 7. The final fractional reduction of H-RDF sample at 1000°C was 93%. In the case of H-RDF sample, flow rates of generated gases became the maximum values in around 20–50 s except CO. CO was detected in the first period of the reaction and CO was detected in the middle and last periods in about 90–240 s. The flow rate of CO had another peak in about 170 s besides earlier one. The former and latter peaks are supposed to correspond to the thermal decomposition of RDF and the reduction of iron oxide, respectively.

Gas generation behavior in the reduction experiments of H-PE and H-RDF samples at 1200°C are also shown in Figs. 8 and 9, respectively. The final fractional reductions of H-PE and H-RDF samples at 1200°C were 63% and 100%, respectively. In addition, the final fractional reductions of H-PE and H-RDF samples at 1300°C were 75% and 100%, respectively. An increase of the reaction temperature from 1000 to 1200°C led to increases of H$_2$ and CO gas volumes in all samples. In the case of H-PE sample, CO was already detected in the first period of the reaction at 1200°C differ from the reaction at 1000°C. In the case of
H-RDF sample, the flow rate of CO had only one peak at 1200°C, though the flow rate of CO had two peaks at 1000°C. This is probably because the peak of reduction moved toward short time side by an increase of the reduction rate of iron oxide with increasing temperature.

### 3.3. Comparison of Conversion Ratios between Thermal Decomposition and Reduction

Figure 10 shows \( CR_H \) by thermal decomposition of PE sample and reduction of H-PE sample. ‘Others’ in the figure means higher order of hydrocarbon which were not measured in this work, char and tar. The conversion ratio into \( H_2 \) by reduction was larger than that by thermal decomposition. The conversion ratios into \( H_2 \) by reduction and thermal decomposition reached 60–70% at 1300°C.

Figure 11 shows \( CR_H \) by thermal decomposition of RDF sample and reduction of H-RDF sample. In the case of RDF, the conversion ratio into \( H_2 \) by thermal decomposition and that by reduction were almost the same. The conversion ratio into \( H_2 \) increased with increasing temperature. The occurrence of iron oxide reduction by \( H_2 \) was confirmed because the conversion ratios into \( H_2O \) by reduction were 3–10% larger than those by thermal decomposition. The final fractional reductions increased with increasing temperature. Nevertheless the conversion ratios into \( H_2O \) of H-PE sample and those of H-RDF sample decreased by 6% and 2% with increasing temperature from 1000 to 1200°C, respectively. These results indicated that reduction of \( H_2O \) to \( H_2 \) by the water gas reaction (Eq. (3)) was enhanced with increasing temperature.

\[
H_2O(g) + C(s) = H_2(g) + CO(g) \quad \text{..................(3)}
\]

Figure 12 shows \( CR_C \) by thermal decomposition of PE sample and reduction of H-PE sample. In thermal decomposition of PE sample, the conversion ratio into ‘Others’ increased and the conversion ratios into hydrocarbon gases decreased with increasing temperature. The reason for the decrease of hydrocarbon gases is that decomposition of hydrocarbon gases into \( H_2 \) and carbon was promoted by increasing temperature. In reduction of H-PE sample, the conversion ratio into ‘Others’, hydrocarbon gases and \( CO_2 \), decreased, and the conversion ratio into \( CO \) increased with increasing temperature. These results indicated that deposited carbon was consumed by the water gas reaction (Eq. (3)), the Boudouard reaction as written in Eq. (4) and
the reduction of iron oxide as written in Eq. (5).

\[
\text{CO}_2 (g) + C (s) = 2\text{CO} (g) \quad \text{(4)}
\]

\[
\text{FeO}_n (s) + C (s) = \text{FeO}_{n-1} (s) + \text{CO} (g) \quad \text{(5)}
\]

Figure 13 shows \(\text{CR}_c\) by thermal decomposition of RDF sample and reduction of H-RDF sample. The conversion ratios into CO and \(\text{CO}_2\) by reduction of H-RDF sample are 2–4 times and about 2 times as large as those by thermal decomposition of RDF sample, respectively. The conversion ratio into CO by reduction reached more than 80% at 1300°C.

### 3.4. Effect of Fixed Carbon on Reaction Behavior of Iron Oxide Mixtures

External view and macrostructure of cross section of H-PE and H-RDF samples after reduction at 1200°C are shown in Fig. 14. In the case of H-PE sample, metallic iron existed in the external part of the sample and FeO existed in the internal part of the sample. This result suggests that the reduction reaction progressed mainly in the external part of the sample. The final fractional reductions of H-PE and H-RDF were 63% and 100%, respectively. This difference indicates that reaction behavior of waste plastic materials and iron oxide mixtures depends on kinds of waste plastic materials.

In the first period of the reaction of H-PE and H-RDF samples, the temperature at the sample surface is higher than that at the inside of the samples, because the thermal decomposition of plastic materials is an endothermic reaction. Therefore, the reduction reactions (Eqs. (6), (7)) of iron oxide by \(\text{H}_2\) and CO (only \(\text{H}_2\) in the case of H-PE sample), which generated by the thermal decomposition of plastic materials, progress mainly near the surface of the samples.

\[
\text{FeO}_n (s) + \text{H}_2 (g) = \text{FeO}_{n-1} (s) + \text{H}_2\text{O} (g) \quad \text{(6)}
\]

\[
\text{FeO}_n (s) + \text{CO} (g) = \text{FeO}_{n-1} (s) + \text{CO}_2 (g) \quad \text{(7)}
\]

When metallic iron generates near the surface, it would be a catalyst for the thermal decomposition of hydrocarbon gases and carbon deposits near the surface by the thermal decomposition of hydrocarbon gases. This deposited carbon promotes the generation of \(\text{H}_2\) and CO by the water gas reaction (Eq. (3)) and the Boudouard reaction (Eq. (4)). As the results, the reduction reactions progress further near the surface of the samples.

In the middle period of reaction of H-PE sample, even if the temperature at the inside of the sample reaches high enough temperatures for the reduction of FeO to metallic iron, most of PE has already decomposed because the evaporation temperature of PE is much lower (about 500°C) than the adequate temperatures for the reduction reaction. Further reduction reaction by the carbon would not take place because decomposition of PE does not generate char (decomposed carbon) as mentioned in Sec. 3.1. Therefore, the reduction reaction at the inside of the sample stagnates as shown in Fig. 14.

On the other hand, in the middle period of reaction of H-RDF sample, a large amount of char which is fixed carbon remains in the sample differ from the case of H-PE sample as mentioned in Sec. 3.1. Therefore, the water gas reaction (Eq. (3)) and the Boudouard reaction (Eq. (4)) can progress more actively and larger volumes of CO and \(\text{H}_2\) are generated than H-PE sample. This CO gas reduces iron oxide. Consequently, in the H-RDF sample, the reduction reaction at the inside of the sample does not stagnate and higher fractional reduction is obtained than H-PE sample even at the same temperatures.

From these results, when waste plastic materials are used as a reducing agent, plastics which contains large amount of fixed carbon are suitable to obtain a high fractional reduction.

### 4. Conclusions

The applicability of waste plastic materials in the carbon composite method was investigated by examining the reaction behavior of the waste plastic materials and iron oxide mixtures. Following results were obtained.

1. \(\text{H}_2\) and \(\text{CH}_4\) were mainly obtained by thermal decomposition of PE at 1000–1300°C. \(\text{H}_2\) was mainly obtained with some of CO by thermal decomposition of RDF.

2. Reduced iron was obtained by heating the PE/RDF and iron oxide mixtures, and a higher fractional reduction was obtained with increasing temperature. In particular, the fractional reductions of the mixtures containing RDF at
1,200°C and 1,300°C were 100%.

(3) In the case of PE and iron oxide mixtures, the reduction reaction of iron oxide stagnated because char (decomposed carbon) did not remain inside of the sample. On the other hand, in the case of RDF and iron oxide mixtures, the reduction reaction of iron oxide progressed well because a large amount of char generated by thermal decomposition of RDF remained inside of the sample.

(4) The conversion ratio into H₂ was almost the same between thermal decomposition of waste plastic materials and reduction of waste plastic materials and iron oxide mixtures. The conversion ratios into H₂ reached 60−70% at 1,300°C. However, the conversion ratio into CO by reduction was larger than that by thermal decomposition. The conversion ratios into CO reached 70−80% at 1,300°C.

(5) When waste plastic materials are used as a reducing agent, plastics which contains large amount of fixed carbon are suitable to obtain a high fractional reduction.

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