Reduction Behavior of Hematite Composite Containing Polyethylene and Graphite with Different Structures with Increasing Temperature

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Plastic wastes can play the significant role of reductants for iron oxides by supplying reducing gases, e.g., $\text{H}_2$ and $\text{CO}$, through pyrolysis. However, there is a problem that the thermal degradation temperature of plastics is significantly lower than the reduction temperature of iron oxide. If a large temperature difference can be formed within the composite granule, the reducing gases thus released can be used as reductants. Therefore, in this paper, the reduction behavior of the composites prepared by using hematite, graphite, and polyethylene regents with different compositions and structures was examined in order to understand the reduction behavior and to attain a high utilized ratio of polyethylene to reduction. Reduction experiments of the composites were carried out under an inert gas flow, and gases formed during reduction were continuously analyzed. The reduction degree of hematite was calculated using the concentration of these gases. Further, micro- and macrostructures of the reduced composite were observed. The addition of polyethylene to a hematite composite containing polyethylene and graphite led to a decrease in the final reduction degree, under the same ratio of carbon to oxygen in the composite. This indicates that the contribution of polyethylene to the reduction reaction was limited. This is because the crack formation enhanced the direct outward flow of the composite without contributing to the reduction reaction. In contrast, the double-layer composite, in which the polyethylene content in the inner layer is larger than that in the outer, shows an effective utilization of polyethylene as compared to the homogeneous composite.

KEY WORDS: reduction; hematite; graphite; composite structure; plastics addition.

1. Introduction

Recently, the reduction of carbon dioxide that is emitted by various sources has become a subject that concerns the entire world, as it is necessary for the prevention of global warming. In the ironmaking process, an increase in the production rate and a decrease in the reduction temperature of iron ores are important for conserving energy, which in turn leads to a decrease in the carbon dioxide emission. However, since the efficiency of conventional processes with blast furnaces has been already reached at nearly the maximal values, a drastic improvement in energy consumption seems to be difficult. Therefore, it is required to develop an innovative ironmaking process. In particular, the utilization of a carbon–iron oxide composite has attracted attention. For example, FASTMET process, which uses the carbon–iron oxide composite, can produce reduced iron within approximately 15 min. There are a number of reports about the reduction behavior of the composite containing carbonaceous materials and iron oxide. In contrast, approximately 10 million tons of plastic waste, mainly polyethylene (PE) and polypropylene, is annually generated in Japan. Approximately 20% of this waste is reused through material- and chemical-recycle schemes. Since the remaining 80% is incinerated or sent to landfills, it is desired to utilize this portion of the waste more effectively. In fact, plastic wastes have great potential as a reductant for iron ores because their major elements are hydrogen and carbon. If they can be effectively used in the ironmaking process, the total CO$_2$ emission caused by fossil fuels will decrease because the amount of plastic waste incinerated simply by a waste treatment will decrease. Therefore, plastic wastes are already used as a raw material in the production of coke or directly injected to the raceway of a blast furnace after pulverization. However, only approximately 0.3 million tons per year of plastic waste is used in this manner. In order to increase the amount of plastic wastes used in the ironmaking process, other methods to use them should be considered. The authors focus on the utilization of plastic wastes as reductants in the carbon–iron oxide composite.

There are a few reports on the utilization of plastics as raw materials in the composite. Hasegawa et al. reported that the gasification, reduction, and melting behavior of the iron oxide composite with PE and wood chip at the temperatures of 1673–2073 K. Sample of 6 g were charged into
the crucible for a period of 14 min. The gas species generated were mainly CO and H₂. However, it may be difficult to realize such a rapid heating condition for large amount of materials. Ueki et al. reported the weight change in the hematite composite with PE and refuse-derived fuel (RDF) during heating at 1273 and 1473 K. Reduction degrees of the PE/hematite composite with C/O (molar ratio of carbon to oxygen) of 1.0 and 2.0 at 1473 K were 75% and 80%, respectively. However, the reduction and gasification behaviors of the composite before reaching the aiming temperature are not clear because of the rapid heating.

Thermal degradation of PE occurs in the temperature range of 650–800 K, which is significantly lower than that for the reduction reaction of iron oxide. When the composite is heated, the temperature in the composite rises by the heat transfer from the surface to the inside of the composite. Such a heat transfer is inhibited by the endothermic reactions, i.e., reduction of iron oxide and pyrolysis of plastics, and also by the gas flow outward the composite due to the formation and volume expansion of gas as shown in Fig. 1. These phenomena create a large temperature distribution within the composite. It means that plastics have a certain potential to be used as a reductant of the composite because H₂ and CO gases generated at the inner part of the composite are able to reduce iron oxide in the outer part.

In this study, the reduction of iron oxide in the composite under a high heating rate which made a temperature distribution was focused on. PE was used as a carbonaceous material because it was a major component of plastic wastes and had a relatively high thermal degradation temperature as compared to other plastics such as polystyrene. Graphite was additionally utilized in order to obtain a high reduction degree. It is because the reduction of iron oxide in a composite containing only PE will be difficult to complete as reported by Ueki et al. Furthermore, a double-layer structure has been designed through which plastic wastes can be utilized for reduction more effectively. This composite contains inner and outer layers. The former contains a higher ratio of plastic than the latter. A series of the reduction experiments was conducted using such composites. Based on the results, the effect of the distribution of reductants in the composites was discussed.

2. Experimental

A mixture of hematite (average diameter: 2.6 μm), medium density polyethylene (PE, average diameter: <250 μm, 0.94 g/cm³), and graphite (average diameter: <45 μm) reagents was used for the preparation of composite samples. The amount of PE and graphite added varied from 0 to 13.0 mass% (C/O=0.00, 0.10, 0.20, 0.42) and from 0 to 18.0 mass% (C/O=0.00–0.97), respectively. Composite samples with weight, diameter, and height of 3 g, 18 mm, and approximately 5 mm, respectively, were prepared by the following method. PE, graphite, and hematite powders were mixed well. The powder mixture was first heated up to 423 K and kept for 900 s in a die and then press-shaped under a pressure of 98 MPa at the same temperature. Subsequently, it was cooled with loading, and a uniform composite was obtained.

For the preparation of the inner layer (total C/O=1.15) of a double-layer composite, hematite was first mixed with 8.7 mass% PE (C/O=0.42) and 12.9 mass% graphite (C/O=0.73), respectively. Then, the press-shaped sample with a diameter and height of 10 mm and 6 mm, respectively, was prepared by the hot-pressing method described above. The outer layer was prepared from a powder mixture, whose composition is shown in Table 1. In order to discuss the structure difference, the total C/O value of the double-layer composites was 0.64 and 0.73, though the reduction reaction did not complete under such C/O values. The inner layer was set at the center of the double-layer composite. The double-layer composites with a diameter of 22 mm were thus prepared. Additionally, a uniform composite with the same size and a total C/O value was prepared for comparison with the double-layer composite samples.

The composite sample was set in a fused silica tube, as shown in Fig. 2, and Ar gas was flowed. Then, it was heated up to 1427 K with a heating rate of 1.3–3.7 K/s using an infrared image furnace. It was cooled down after holding the sample at 1427 K for a certain amount of time. The temperature was measured at the point where was a height of 1 mm from the composite by the Pt/Pt–13%Rh thermocouple. The concentrations of CO and CO₂ in the outlet gas were continuously measured using infrared gas analyzers. The concentrations of CO, CO₂, H₂, H₂O, CH₄, C₂H₄, and C₂H₂ were also measured by gas chromatography. In the chamber, a spacer made of fused silica was set in order to minimize the dead space volume. The reduction degree of hematite was calculated using the change in the composite weight and the generation rates of CO, CO₂, and H₂O gases. The micro- and macrostructures of the composite sample after reduction were observed using an optical microscope.

| Table 1. Inner, outer, and total C/O values of the prepared composite. |
|-----------------|-----------------|-----------------|-----------------|-----------------|
|                 | Inner           | Outer           | Total           |
|                 | C/O            | C/O            | C/O            | C/O            |
| Uniform         |                |                |                |                |
| l               | 0.12           | 0.52           | 0.12           | 0.52           | 0.64           |
| Double-layer    |                |                |                |                |
| 2               | a              | 0.42           | 0.73           | 0.42           | 0.73           |
| b               | 0.42           | 0.73           | 0.10           | 0.50           | 0.63           |
3. Results

3.1. Reduction Behavior of Uniform Composite

Changes in the generation rates of gases from the uniform composite heated at the rate of 1.3 K/s are shown in Fig. 3, together with the temperature change. The results shown in Figs. 3(b) and 3(c) are for the uniform composites containing 10 mass% PE and 8.6 mass% graphite, respectively. The C/O values of both composites were 0.42. The generation of CO2, H2, and H2O gases from the composite containing PE begins at approximately 700 K. It seems that CO2 and H2O gases were generated by the reduction reactions of iron oxide with carbon and hydrogen caused by PE. Some peaks are observed in the curve of CO2 concentration, and the curve shows the maximum value at approximately 1050 K. CO gas is also generated at approximately 750 K, and the peak value is reached at approximately 1050 K. The amount of H2 generated is approximately ten times lower than that of CO2. CH4, C2H4, and C2H6 gases were also generated from the composite at temperatures ranging from 700 to 900 K. No gas is generated above 1200 K because the pyrolysis of PE was completed by that temperature. The amount of carbon in the generated gases was less than half of the initial carbon content in the composite, but a considerable amount of tar remained in the tube after the experiment. These results indicate that the undetected carbon was condensed as tar. In contrast, in the case of the composite with graphite, the generation of CO2 and CO begins at 1070 and 1250 K, respectively. The amount of CO gas concentration increases abruptly at approximately 1400 K. The reason for this increase may be that a solution loss reaction was activated by the catalysis of metallic iron, which forms by the reduction of iron oxide. The total amount of detected gas from the composite with graphite was approximately five times higher than that with PE. The obtained reduction degrees of the composite with PE and graphite to the C/O value were 0.42 and 0.13, respectively. The formation of gas was found to occur in two steps. The first step begins at approximately 700 K, and it almost ends at 1200 K. The peak temperature that corresponds to the CO and CO2 formation peaks is approximately 1100 K, although the CO2 concentration is higher than the CO concentration. This behavior is similar to that of the hematite composite that contained only PE. It implies that the first step was caused by PE. The reaction for gas generation starts again at approximately 1200 K, which is considered to be the second step. This gas generation is caused by graphite because the gas generation caused by PE was completed below 1200 K. However, this gas generation behavior is different from that observed in the case of the addition of only graphite. For example, CO2 gas generation at 1200 K as shown in Fig. 3(c) cannot be obtained from the result shown in Fig. 4. The difference obtained between the composite with graphite addition only and that with the mixture of PE and graphite can be attributed to the different reduction stages as described below. The reduction degree of this uniform composite was approximately 40%, which became twice higher than that with only PE addition.
Figure 5 shows the changes in the partial pressure ratio of CO to CO\textsubscript{2}, (CO)/(CO+CO\textsubscript{2}), of the outlet gas with an increase in temperature drawn on the phase diagram of the Fe–O system. The uniform composites used are 10mass% PE (C/O=0.42, A), 10mass% PE–2.3mass% graphite (C/O=0.55, B), 5mass% PE–6.7mass% graphite (C/O=0.55, C) and 8.6mass% graphite (C/O=0.42, D). (CO)/(CO+CO\textsubscript{2}) obtained from the composites A–C with added PE begins to increase gradually at approximately 700 K. It abruptly increases at 900 K and reaches the coexistence line of magnetite and wustite at approximately 1000 K. Then, it moves on the line with increasing temperature. All composite with added PE exhibited this behavior. This indicates that the reduction reaction of magnetite controls (CO)/(CO+CO\textsubscript{2}).

Figure 6 shows the microstructure of the reduced composite B containing 10 mass% PE and 2.3 mass% graphite after keeping the composite in the furnace for 650, 740, and 1200 s at 1100, 1200, and 1427 K, respectively. Two oxide phases of magnetite and wustite are observed at 1100 K, and this agrees with the results obtained from the gas analysis. (CO)/(CO+CO\textsubscript{2}) of the composite A without the added graphite rapidly decreases at approximately 1100 K since the generation of CO and CO\textsubscript{2} gas caused by PE has been completed at this temperature as shown in Fig. 3(b). In contrast, (CO)/(CO+CO\textsubscript{2}) of the composites B and C with added graphite is observed in the region of an FeO single phase. From the microstructure observation, it was concluded that an FeO single phase also existed at 1200 K. After reaching the holding temperature, the ratio reaches the coexistence line of wustite and metallic iron. In the microstructure given in Fig. 6(c), metallic iron is partially observed together with wustite.

On the other hand, (CO)/(CO+CO\textsubscript{2}) generated from the composite D without the added PE begins to increase at approximately 1200 K because CO gas did not generate below this temperature as shown in Fig. 3(c). At 1300 K, (CO)/(CO+CO\textsubscript{2}) reaches the coexistence line of magnetite and wustite. The difference of the CO gas generation behaviors between the uniform composites A–C with the added PE and D without the added PE at temperatures ranging from 1250 to 1400 K, described above, can be considered to be as follows. The reduction reaction of the composite A–C with added PE proceeded to the stage of an FeO single phase because the reduction of hematite and magnetite had already occurred by PE at a low temperature. In contrast, the reduction of the composite D without added PE began at approximately 1200 K and then, FeO started to form at approximately 1300 K.

Figure 7 shows the relation between reduction degree and C/O of the uniform composite containing various amounts of PE and graphite. The reduction degrees of the composites containing 0, 2.5, 5, and 10 mass% PE increase linearly with increasing C/O values. In contrast, the addition of PE decreases the reduction degree. The contributions of PE to the C/O values of the uniform composites containing 0, 2.5, 5, and 10 mass% PE were 0, 0.1, 0.2, and 0.42, respectively. The C/O values required for the complete reduction of these samples were at least 0.80, 0.81, 0.92, and 1.18, respectively. The effect of C/O attributed to PE on minimum C/O required to complete the reduction reaction is shown in Fig. 8. Assuming that PE had the same effect on the reduction reaction as graphite, the minimum C/O should be constant. Moreover, if iron oxide in the composite was reduced by the hydrogen generated by the ther-

![Fig. 5. Change in partial pressure ratio of CO to CO+CO\textsubscript{2} in outlet gas generated from the composites with an increase in temperature on the phase diagram of Fe–O system.](image)

![Fig. 6. Microstructure of composites containing 10 mass% PE and 2.3 mass% graphite after kept in the furnace for various time periods, a) 650 s at 1100 K, b) 740 s at 1200 K, and c) 1200 s at 1427 K.](image)

![Fig. 7. Relation between reduction degree and molar ratio of carbon to oxygen (C/O) of the uniform composite containing various amount of PE and graphite together with metallization ratio of 10mass% PE–graphite composite under a heating rate of 1.3 K/s.](image)
mal degradation of PE, the minimum C/O may decrease. However, the minimum C/O increases with increasing C/O attributed to PE. This indicates that the utilization ratio of PE for the reduction reaction decreased with increasing amount of added PE. Furthermore, there is a possibility that an increase in the amount of added PE decreased the utilization ratio of graphite for the reduction. Figure 9 shows the macrostructure of the composites with 2.5 and 10 mass% PE. Many small cracks are observed in the case of the composite with 2.5 mass% PE. In contrast, not only small cracks, but also a few large ones are observed in the case of the composite with 10 mass% PE. It is estimated that the reducing gas generated was not utilized effectively to reduce iron oxide because these gases escaped to the outward of the composite through the large cracks. Therefore, the reduction degree of the composite with a high amount of added PE became lower. It means that the control of crack formation is essential for the effective utilization of PE in the reduction of iron oxide composites.

3.2. Double-layer Composite

In order to attain a high utilization ratio of carbon by the effective use of the temperature distribution and the control of gas flow in the composite, three kinds of the composite structures with different PE amounts in the inner and outer layers, as shown in Fig. 10, were utilized. Figure 11 shows the relation between the reduction degree and C/O attributed to PE. The total C/O was 0.64. Open square plots illustrate the reduction degree of the uniform composite calculated by linear approximation using the results of reduction degree shown in Fig. 7. The reduction degree of the uniform composite with a diameter of 18 mm under the heating rate of 1.3 K/s decreases with increasing C/O attributed to PE. The solid square plot shows the result of the uniform composite with a diameter of 22 mm under the heating rate of 3.7 K/s. The reduction degree has almost the same value as that on the dashed line under the same C/O, though the composite size and heating rate were different. An increase in composite size and heating rate will lead to the ex-
pansion of the temperature distribution in the composite. Therefore, the reducing gas generated from PE would be utilized effectively for the reduction at high temperature in the outer layer. However, there was no such effect observed under these experimental conditions.

The reduction degree of the double-layer composite 1 (DL1) is lower than that of the uniform composite under the same C/O attributed to PE. Furthermore, the reduction degree of DL1 is lower than that of the uniform composite, which has higher PE content than DL1, showed by a solid square plot in Fig. 11, although the reduction degree increases with decreasing PE content, as shown in Fig. 7. Macrostructures of uniform and double-layer composites are also shown in Fig. 10. As compared to the case of the uniform composite, in the case of DL1, larger cracks form at the outer layer. The outer layer of DL1 had lower porosity than the uniform composite because it had no added PE. It was difficult for the gas generated rapidly in the inner layer to pass through the outer layer. Thus, the pressure in the inner layer of DL1 increased. As a result, the composite showed cracks at the interface between the inner and the outer layers. Therefore, the reducing gas that was generated in the composite escaped without being any utilized effectively.

On the other hand, the reduction degree of the double-layer composite 2a with added PE in the outer layer (DL2a) is higher than that of the uniform composite. After the gasification of PE in the outer layer, porosity of the outer layer of DL2a is higher than that of DL1. High porosity keeps the path for the gas generated in the inner layer. Accordingly, it prevents the formation of large cracks in the outer layer, as shown in Fig. 10(c). Figure 12 shows the relation between the reduction degree and C/O together with the results of the uniform composite shown in Fig. 7. Total C/O attributed to PE was 0.12. The structure design of DL2b was similar to DL2a, but the amount of graphite in the outer layer was slightly higher than that of DL2a. The reduction degree of DL2 is higher under the same C/O than that of uniform composite. As a result, C/O required to complete reduction of iron oxide in DL2 can calculate as 0.75, which is 0.05 lower than that of uniform composite without added PE. It indicates that total carbon amount utilized for the reduction of iron oxide can reduce by approximately 6%. Therefore, it can be concluded that waste plastics can be effectively utilized as a reducing agent for iron oxide by using a composite with appropriate structure that can prevent the formation of large cracks and keep the flow path outside the composite during reduction.

4. Conclusions

The reduction behaviors of the composite of hematite containing graphite and polyethylene powders with different structures were investigated, and the following results were obtained.

1. For the uniform composite, the reduction reaction started at a low temperature of approximately 700 K under the heating rate of 1.3 K/s. Above 1 000 K, the reduction reaction proceeded with discharging CO and CO2 gases, whose concentrations were nearly equal to the equilibrium concentration between FeO and Fe3O4. FeO was reduced to metallic iron at the holding temperature of 1 427 K.

2. The reduction degree of the uniform composite with constant amount of added polyethylene increased with increasing the value of molar ratio of carbon to oxygen. However, the addition of polyethylene to the uniform composite decreased the reduction degree under the same ratio of carbon to oxygen in the composite. It means that the contribution of polyethylene to the reduction reaction was limited. The reason is that the reducing gas generated from polyethylene was not utilized effectively for the reduction of iron oxide since these gases escaped to the outward of the composite through the large cracks which formed during heating.

3. High reduction degree was obtained by using a double-layer composite whose polyethylene content was concentrated in the center of the composite with slight addition of polyethylene in the outer layer so that the generated gas was effectively utilized for the reduction and a large crack formation could be prevented in the outer layer.

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