

REDUCTION AND GASIFICATION BEHAVIOR OF THE COMPOSITE OF COAL AND IRON ORES CONTAINING DIFFERENT CONCENTRATION OF COMBINED WATER ¹

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Abstract

Due to rapid increase of world steel production, steel industry is facing two difficult tasks to solve simultaneously. These are the reduction of CO₂ emissions and the effective use of low-grade iron ore resources with relatively high concentration of combined water. Lowering the reduction temperature of iron oxide using a carbon-ore composite is promising ways to solve the former problem. The latter is mainly concerning to the Australian pisolite and marramamba ores. In this study, effects of particle size and the concentration of combined water on the reduction and gasification behaviors of the composite were examined. The coal/ore composite sample was heated up to 1573 K under Ar gas flow. The changes in the reduction and gasification degrees were calculated using the concentration of the generated gases. The peak of CO gas generation from the composite using pisolite and marramamba ores was obtained at about 1173 K, though there was no peak for hematite ore. Below 1373 K, the gasification degree increased with increasing the combined water concentration in the ore. It appears that the gasification reaction was accelerated by the catalytic effect of metallic iron formed by the reduction. Accordingly, the higher reduction degree was obtained below 1373 K.

Key words: Reduction of CO₂ emission; Iron ore resources; Coal; Reduction of iron oxide.

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1 INTRODUCTION

Last year, the crude steel production in Japan had reached to the 130 million ton level in response to expanding world demand, which was mainly attributable to China. The price of raw materials and energy sources like iron ore and coal, respectively on the world markets soars like never before. In addition, the supply situation of these materials becomes worse. It becomes difficult to obtain high-grade iron ore such as hard hematite ore at low cost. Furthermore, it is urgently required to reduce greenhouse gas emissions from iron and steel industry since it emits a large amount of carbon dioxide. Lowering the thermal reserve zone temperature in blast furnace by the activation of gasification reaction and reduction of iron oxide is one of promising ways to solve this problem. Especially, the utilization of a carbon-iron ore composite has attracted attention. There are many reports about the reduction behavior of the composite containing carbonaceous materials and iron ore. Kasai *et al.* reported that reduction of iron ore in the composite, which was made by a briquetting method by the use of thermal plasticity of coal at relatively lower temperature in comparison with the agglomeration temperatures of sinter and pellet.⁽¹⁾ The utilization of such composites makes the thermal reserve zone temperature decrease in comparison with the sinter using the blast furnace simulator. Rao investigated the reduction kinetics of the mixture of hematite and carbon and the effects of carbon particle size, the holding temperature, and the mixture ratio of hematite and carbon on the reduction behavior.⁽²⁾ And it was reported that the solution loss reaction constitutes the rate-determining step for the overall process. Huang *et al.* reported a fundamental study of reduction in mixtures of iron ore and coal by indirect heating. They concluded that the rate-determining step of the overall reaction is considered to be heat transfer.⁽³⁾ On the other hand, it is available countermeasure for raw materials problem to develop the method of the effective utilization of low-grade iron ores, which contain higher amount of gangue and combined water. However, there has been no systematic investigation focused on the effect of the gangue composition and concentration of combined water of iron ores on their carbothermic reduction behaviors. In this study, effects of particle size and the concentration of combined water of different iron ores on the reduction and gasification behaviors of the composite were examined.

2 MATERIALS AND METHODS

Five kinds of iron ores, which are one hematite (H), two marramamba (M), and two pisolite (P) ores with three ranges of particle sizes (< 44, 44 - 105, 105 - 250 μm) were used. The chemical composition of these ores is shown in Table 1. Noncoking coal with the powder size of < 44 μm (VM: 36%, Fixed Carbon: 56%, Ash: 8%) was selected as carbonaceous reductants. A well-mixed ore and coal powder was press-shaped under a pressure of 9.8×10^7 Pa at room temperature. The composite sample with a diameter, and height of 10 mm, and 10 mm, respectively was obtained. The mixture ratio defined as C/O, which was the molar ratio of fixed carbon in the coal to oxygen of iron oxide was 0.8. The coal/ore composite sample was set in the chamber made of fused silica under the Ar-5%N₂ flow with the rate of 8.33×10^{-6} Nm³/s as shown in Figure 1. Then, it was heated up to 1573 K with the heating rate of 0.33 K/s using an infrared image furnace. The temperature was measured at the point where was a height of 1 mm from the composite by the Pt/Pt-13%Rh thermocouple. In the chamber, a spacer made of quartz was set in order to decrease

the dead space volume. 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 C₂H₆ were also measured by gas chromatography. The reduction degree of iron oxide was calculated using the change in the amounts of generated CO, CO₂, and H₂O gases. The gasification degree was also calculated using the change in the amount of CO, CO₂, and hydrocarbon gases. The remained carbon content in the composite after experiment was analyzed. The micro- and macrostructure of the composite sample were observed using an optical and scanning electron microscopes.

Table 1. Chemical composition of iron ores used.

	T-Fe	SiO ₂	Al ₂ O ₃	LOI
	(mass%)			
H1	68.0	1.3	0.7	0.5
M1	63.8	2.7	1.8	4.2
M2	59.9	3.7	2.7	7.8
P1	59.4	5.0	1.2	8.7
P2	57.2	5.5	2.5	10.1

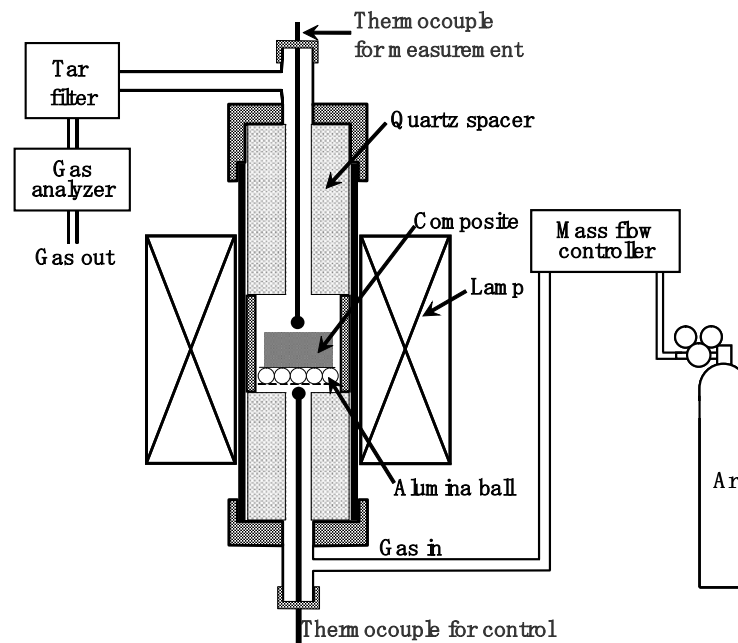


Figure 1. Schematic diagram of experimental apparatus for the reduction of composite

3 RESULTS AND DISCUSSION

3.1 Effect of Iron Ore Particle Size in the Composite on Reduction Behavior

Figure 2 shows the changes in the amount of gases generated from the coal/H1 composites with different particle size of ore with temperature. The particle sizes are <44, and 105-250 μm, respectively. The amount of gases is described as number of moles per 1 g of iron in the composite. The right axis is used for only CO gas because it showed higher peak value than other gases. Above 700 K, CH₄ gas caused by volatile matter in coal generates, and it shows the peak value at approximately 800 K. C₂H₄ and C₂H₆ were also detected at this period. H₂ and CO₂ sequentially generate from the composite using ore with the particle size of <44 μm and the amount of CO₂ and H₂ shows the peak value at 870, and 1000 K,

respectively. After the gasification of combined water, water vapor generates continuously during heating. These results indicate that the reduction of iron oxide proceeds by carbon and hydrogen caused by volatile matter in coal at such low temperature. The amount of generated CO_2 also shows other peaks at 1173 and 1323 K. The amount of generated CO starts to increase at approximately 1180 K, and it shows the peak value at approximately 1360 K. Then, the amount of generated gases abruptly decreases. The temperatures at which the amount of gas except hydrocarbon gases shows the peak value increase when the particle size of ore is 105-250 μm . Above approximately 1200 K, the ratio of CO to CO_2 generated from the composite using larger particle size ore is higher than that using smaller one. The reason is that the ratio of gasification rate from coal to the reduction rate was relatively-large because the reduction rate of iron oxide decreased by the increase of particle size of iron ore.

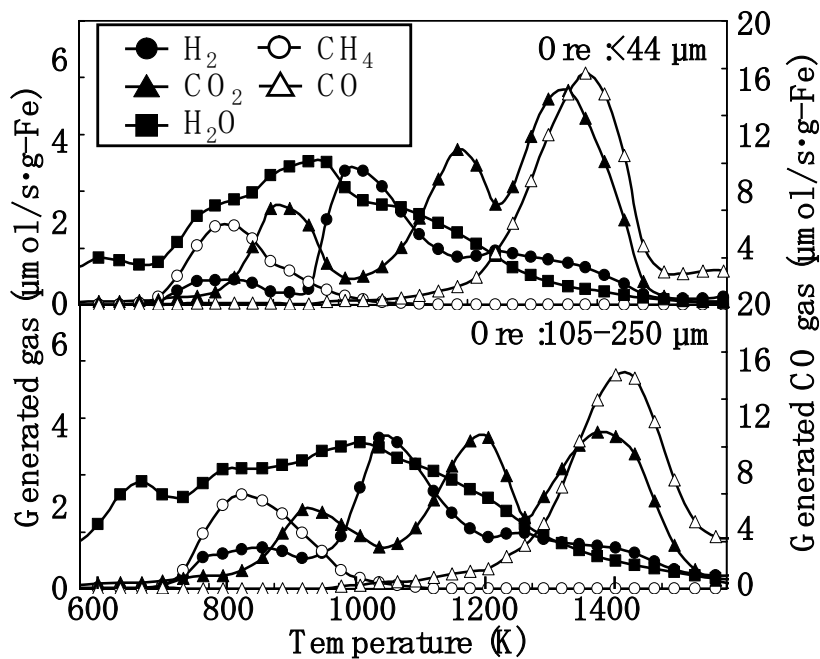


Figure 2. Changes in the amount of gases generated from coal/ore (H1) composites with different ore particle size with temperature.

Temperature changes in the gasification rate from coal/H1 composites with different particle size of ore are shown in Figure 3. There is no difference in the gasification rate that the reaction caused by the volatilization from coal starts from approximately 700 to 1000 K between these particle sizes. The rapid increase of the gasification rate of the composite with the ore particle size of $<44 \mu\text{m}$ starts at 1200 K. This rate shows the maximum value at about 1360 K, and then, it rapidly decreases. The calculated oxygen partial pressure from the generated gases at this temperature range was almost equaled to the equilibrium value between Fe and FeO. It seems that the gasification such as solution loss reaction is activated by catalysis effect of formed metallic iron. The beginning temperature of the rapid increase of the gasification rate increases with increasing the ore particle size, and the maximum rate decreases. The reason is that the temperature at which metallic iron forms decreases with decreasing the particle size of ore.

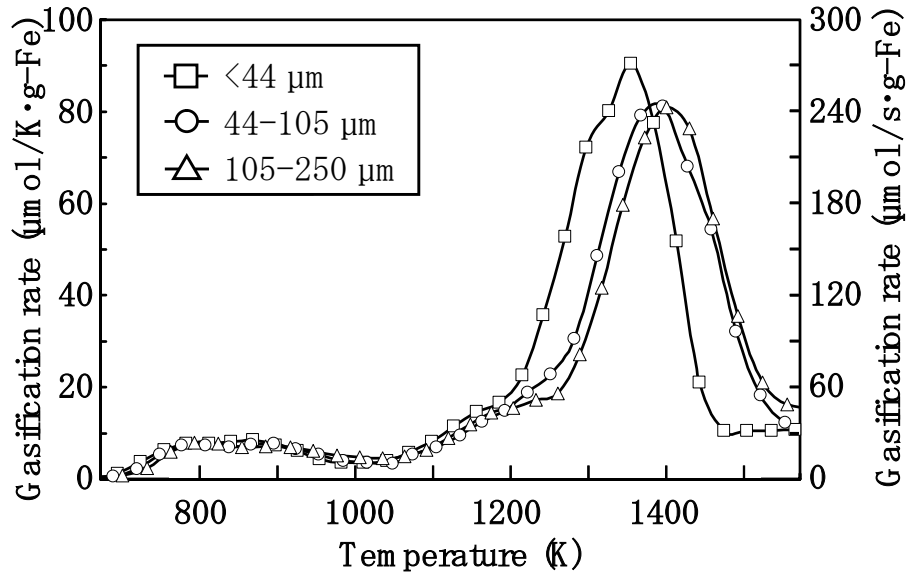


Figure 3. Changes in the gasification rate from coal/ore (H1) composites with different ore particle size with temperature.

Relation between reaction behavior and concentration of combined water

Figure 4 shows the reaction behavior of the coal/ore (H1 and M2) composites whose range of ore powder size is 105-250 μm with the constant heating rate. Amount of water vapor generated from the composite using M2 at the temperature range from 600 to 900 K is much larger than that using H1 since the concentration of combined water in M2 is higher than that of H1. Above 973 K from both composites, amount of water vapor gradually decreases with increasing the temperature. CO_2 generates at low temperature of approximately 700 K, and its amount generated from M2 composite is larger than that from H1. It should be noted that the peak of CO generated from M2 composite is observed at 1160 K, though no peak is observed from H1. Furthermore, amount of CO_2 generated from M2 composite is larger than that from H1 at this temperature range. These results are expected that the reduction reaction of iron oxide in M2 composite proceeds more than that in H1 composite. However, the peak value of CO generated from M2 composite at 1350 K is lower than that from H1. As these results, it is predicted that the different reduction behaviors are obtained.

Changes in the reduction degree of the composites using various iron ores at every 100 K steps from 1073 to 1573 are shown in Figure 5. The powder size range of iron ore used for the composites is 105-250 μm . The dash line means 33% of the reduction degree where metallic iron starts to form. There is the different reduction behavior between various iron ores at the temperature range from 1073 to 1173 K, though no effect of kinds of iron ore below 1073 K is obtained. Especially, high reduction degrees of the composites using marramamba and pisolite ores are obtained. Little difference of the reduction degree change at the range from 1173 to 1273 K is observed. The reduction degrees of the composite using M2, P1, and P2 ores are over 33% at 1273 K because of the advantage of reduction degree change at the range from 1073 to 1173 K. These results indicate that metallic iron formed in the composite at this temperature. On the other hand, highest reduction degree of the composite using H1 ore is obtained at 1473 K.

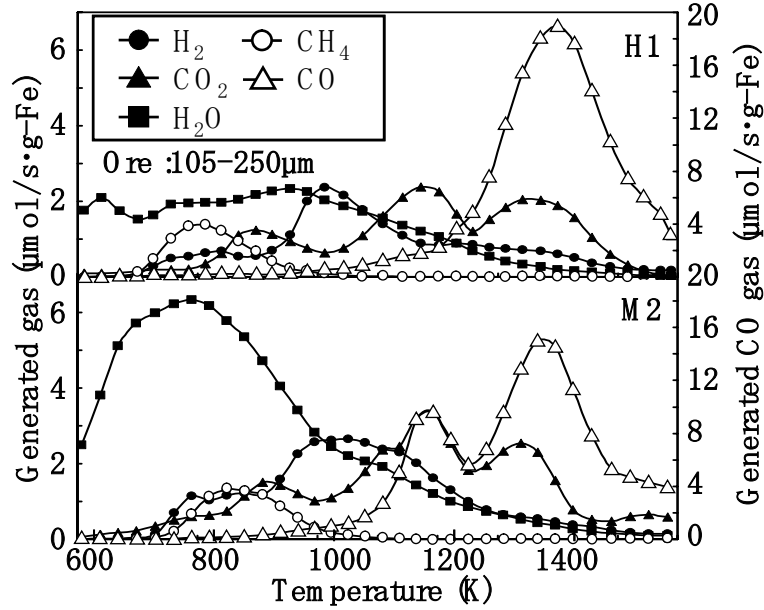


Figure 4. Changes in the amount of gases generated from coal/ore (a) H1 and (b) M2 composites with temperature.

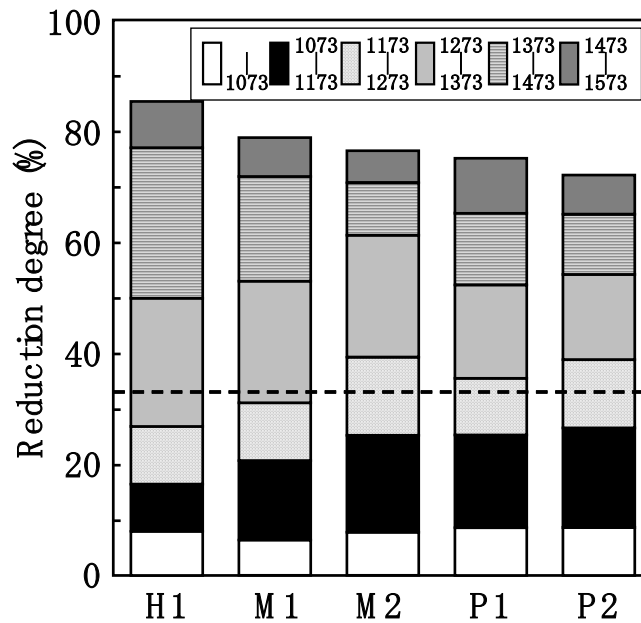


Figure 5. Reduction degree of the coal/ore composites using various kinds of iron ore.

Figure 6 shows the relation between gasification degree and concentration of combined water in the ore at various temperatures from 1073 to 1573 K. The particle size range of iron ore used for the composites is 105-250 μm . At 1073 K, the gasification degree is almost constant with even increasing concentration of combined water, whose trend is same as the reduction degree. At the temperature range from 1173 to 1373 K, the gasification degree increases with increasing concentration of combined water. This trend is prominent at 1273 K. These results indicate that the formation of metallic iron strongly affects the increase of the gasification degree since metallic iron formed in the composite using ore with high concentration of combined water and the catalytic effect appears at 1273 K. A few weight percent of carbon was remained in all composites after experiment. It is

considered that the potential of the gasification is still remained after heating up to 1573 K. However, the gasification degree decreases with increasing concentration of combined water above 1473 K. The reason may be as follows. Amount of SiO_2 in ore increased with increasing concentration of combined water as shown in Table 1. The reduction reaction was retarded by the formation of FeO-SiO_2 slag with low reducing ability at high temperature. Accordingly, an increase of the gasification degree inhibited at such high temperature because the amount of CO_2 generated by the reduction reaction decreased.

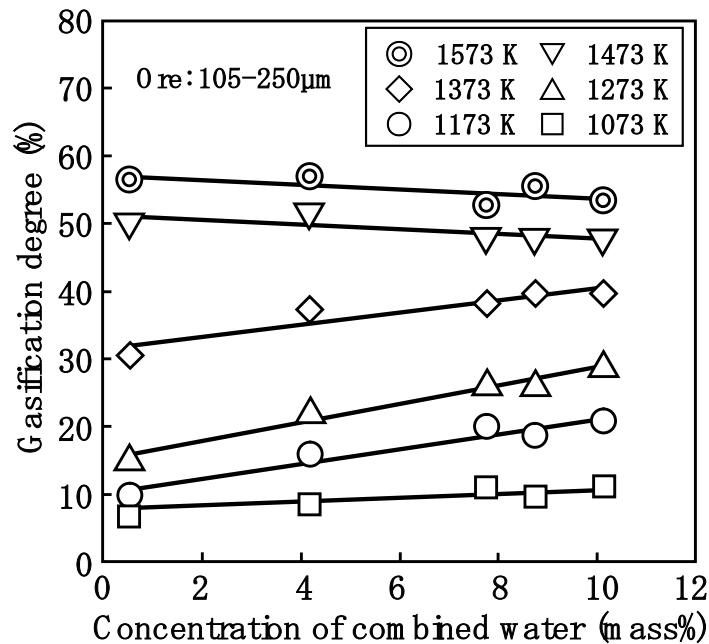


Figure 6. Relation between gasification degree and concentration of combined water in the iron ore at various temperatures.

4 CONCLUSIONS

Effect of iron ore particle size and concentration of combined water in various iron ores on the reduction and gasification behaviors of the composite were examined. The following results were obtained:

1. CO_2 and H_2O gases started to generate from the composite of coal and hematite ore powders at approximately 800 K. It seems to be caused by the reduction of iron oxide. This reduction reaction is mainly caused by the volatile matter contained in coal. The effect of the particle size of the hematite ores was not significant below 1000 K. The peak of the gasification rate appeared at approximately 1360 K. The peak value decreased and the temperature at the peak increased with an increase in the particle size of ore.
2. The concentration peak of CO generated from the composite using ore with high concentration of combined water was observed at approximately 1160 K, while no peak was seen for the composite of hematite ore. In the temperature range from 1173 to 1373 K, the reduction and gasification degrees increased with increasing concentration of combined water of the ores. At higher temperature above 1473 K, however, the reduction degree of the composite of hematite ore became higher. This is because the reduction of the composite using ores with high concentration of combined water retarded at such temperature.

REFERENCES

- 1 Kasai, A., Naito M., Matsui, Y.; Yamagata, Y. Reduction and Carburization of Carbon Composite Iron Ore Hot Briquette on Condition of Increasing in Temperature, *Tetsu-to-Hagane*, v.89, n. 12, pp. 1212-1219, 2003.
- 2 Rao, Y.K. The Kinetics of Reduction of Hematite by Carbon, *Metallurgical Transactions*, v. 2, pp. 1439-1447, 1971.
- 3 Huang, B.H.; Lu, W.K. Kinetics and Mechanisms of Reactions in Iron Ore/Coal Composites, *ISIJ International*, v.33, n.10, pp. 1055-1061, 1993.