Effect of Residual Volatile Matter on Reduction of Iron Oxide in Carbon Composite Pellets

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Abstract
Volatile matter (V.M.) is released in the course of carbonization of coal under a rising temperature condition. The kind and amount of V.M. depend on the kind of coal. Components of V.M. are tar, hydrocarbons (CH₄, C₂H₆, C₂H₄, C₆H₆, C₃H₈), CO, CO₂ and H₂, which are released in this order as a function of carbonization temperature. When the carbonization of coal under a rising temperature condition is interrupted at a maximum carbonization temperature, Tc,max semi-coal-char with residual V.M. is obtained. If some optimum interruption-temperature is chosen, small but most suitable amount of V.M. is retained. When the semi-coal-char thus obtained is heated again under the same rising temperature conditions but up to more than Tc,max, the residual V.M. is released from just around Tc,max. We propose novel iron ore agglomerate bearing such semi-coal-char with some strength in order to decrease the initial temperature for reduction of iron oxide under a rising temperature condition, such as in a blast furnace shaft. The carbonization of Newcastle blend coal under a rising temperature condition was interrupted at Tc,max = 823, 873, 1073, 1173 and 1273 K, to obtain semi-coal-char with some residual V.M. Thus obtained semi-coal-char at Tc,max = 823 K retained much amount of V.M. most of which was H₂. The semi-coal-char was mixed with reagent grade hematite in the mass ratio of one to four, and added with a Bentonite of 1 mass% as a binder. The carbon composite pellets bearing the semi-coal-char were prepared and reduced from room temperature to maximum reduction temperatures, Tr,max = 873, 973, 1073, 1173 and 1273 K, at 3 K min⁻¹ in the nitrogen gas atmosphere. It was confirmed by the gas chromatography of gas generated by reduction of pellets that the carbon composite pellets bearing the semi-coal-char at Tc,max = 823 K had the highest reducibility of the iron oxide; the original Fe₂O₃ was mainly changed to FeO at Tr,max = 973 K and 1073 K, to FeO at 1173 K and to Fe at 1273 K.

Key words
Ironmaking, Carbonization, Volatile Matter, Char, Carbon Composite Pellet

1. Introduction
In recent years, a lot of works have been reported on the carbon composite iron ore agglomerates [1-3]. The carbon composite iron ore agglomerates have higher reducibility than normal iron ore pellets or sinter. Furthermore, there are a lot of advantages, namely, no sintering and utilization of fine ores, dusts, low-grade coal, charcoal or plastics. These advantages lead to high productivity [4] and/or less load to environment. In the past, the carbon composite iron ore agglomerates were generally applied to the rotary hearth furnace process such as FASTMET, INMETCO and COMET in order to produce the direct reduced iron in the country of origin. In these processes advantages such as comparatively faster reduction rate and lower fuel rate had been reported [5]. Recently, the carbon composite iron ore agglomerate is focused on utilizing as raw materials of the blast furnace and shaft furnace. For instance, some cold bonded pellets and briquettes using cements as binders are adopt in the shaft of blast furnaces [6, 7]. However, some problems of slow reduction and low gas permeability occur due to combined water or attached groundwater, high slag ratio and low pellet strength. Therefore, in order to solve these problems, novel carbon composite iron ore agglomerate with high reducibility at low temperatures and some proper strength is needed. Khaki et al reported the improvement of reduction rate of hematite with carbon by the mechanical milling [8]. Kasai et al also reported the carbon composite iron ore hot briquette without a binder [9-11].

On the other hand, when the carbonization of coal under a rising temperature condition is interrupted at a certain temperature, i.e., a maximum carbonization temperature, Tc,max semi-coal-char with residual V.M. is obtained. We propose novel iron ore agglomerate bearing such semi-coal-char with high reducibility at low temperatures having some strength as well. While simple iron ore agglomerate bearing char will start the reduction reaction as solid-solid reaction at somewhat higher temperature, the proposed one will start the reduction reaction as gas-solid reaction at somewhat lower temperature but a little higher than Tc,max under a rising temperature condition. In this work, carbon composite iron oxide pellets bearing the above-mentioned semi-coal-char have been prepared and the effect of residual V.M. on reduction was evaluated.

2. Experimental
2.1 Sample
A Newcastle blend coal (Fixed carbon: 53.4 mass%, V.M.: 41.3 mass%, Ash: 5.3 mass%) as a coal sample and a reagent grade hematite (95 %, Wako Pure Chemical Industries, Ltd.) as an iron oxide sample were used. The Newcastle blend coal had much V.M. of 41.3 mass%. The carbonization of coal under rising temperature conditions were interrupted at certain temperatures, Tc,max = 823, 873, 973, 1073 and 1273 K, to obtain semi-coal-char with some residual V.M. The obtained char was mixed with reagent grade hematite in the mass ratio of one to four. Then, Bentonite of 1 mass% was added to the mixture as a binder in order to strengthen. The particle
size of the mixture was regulated under 45 μm by the sieve. The carbon composite iron oxide pellets bearing such semi-coal-char were prepared.

2.2 Preparation of semi-coal-char

Newcastle blend coal (1000 g) was carbonized partly in order to obtain the semi-coal-char with some residual V.M. A schematic drawing of experimental apparatus is shown in Fig. 1. The coal particles were packed in the top of the reactor, which was heated at 200 K h⁻¹ by a digital thermo-controller. Nitrogen gas with a constant flow rate of 1.67 × 10⁻⁴ (m³ s⁻¹ (s.t.p.)) was passed through the coal-packed bed and mixed with the carbonizing gas to determine each gas flow rate [12]. This gas mixture was filtered through glass wool to remove the tar. The exhaust gas was cooled to condense the water vapor. After the water vapor was captured in the condenser, the carbonizing gas without tar was analyzed by the gas chromatograph (GC14B, Shimadzu Corporation).

![Diagram](image)

Fig. 1. A schematic drawing of experimental apparatus of carbonization; dimensions in mm.

2.3 Reduction of iron oxide

The carbon composite iron oxide pellets bearing the semi-coal-char were kept at 373 K for 24 h in the air in order to remove water. Then, the formed pellets were heated from room temperature to maximum reduction temperatures, Tₑₐ₉ₐₓ = 873, 973, 1073, 1173 and 1273 K at 3 K min⁻¹ in the nitrogen gas atmosphere in order to investigate the effect of residual V.M. on reduction. After reduction, the pellet samples were analyzed by XRD (RINT2500V, Rigaku Corporation) with CuKα line at 40 kV and 200 mA.

3. Results and Discussion

3.1 Carbonization of coal

In order to obtain the semi-coal-char with some residual V.M., the Newcastle blend coal was carbonized from room temperature to Tₑₐ₉ₐₓ = 823, 873, 973, 1073 and 1273 K at 200 K h⁻¹, and kept at Tₑₐ₉ₐₓ until arrival time of 6 h. The obtained variations of main gas flow rates with carbonization time are shown in Figs. 2-5. In Fig. 2, releasing of H₂ gas starts from carbonization temperature Tₑₐ₉ₐₓ = 673 K, and the flow rate reaches the maximum point at Tₑₐ₉ₐₓ except for Tₑₐ₉ₐₓ = 1273 K. H₂ gas flow rate decreases gradually over Tₑₐ₉ₐₓ = 1073 K. From this result, H₂ gas is considered to be released mostly about Tₑₐ₉ₐₓ = 1073 K. In Fig. 3, CO gas flow rate is rising at Tₑ₉₉₉ = 573 K, and the peak is observed between 873 K and 1073 K. Then, CO gas is hardly released at high temperatures over 1173 K. In Fig. 4, releasing of CO₂ gas gradually starts from Tₑₐ₉ₐₓ = 373 K, and stops over 1073 K. Furthermore, total gas volumes generated by carbonization are calculated by integrating these gas flow rates, and are shown in Fig. 5. H₂ gas is released more than any other gas under almost all the conditions. The higher Tₑₐ₉ₐₓ is, the more H₂ gas is released. But, H₂ gas volume is less than the other gas volume at Tₑₐ₉ₐₓ = 823 K. From this result, it was found that the coal char retained much V.M., namely H₂, at Tₑ₉₉₉ = 823 K. In consideration of these, the semi-coal-char with some residual V.M. could be prepared by controlling Tₑₐ₉ₐₓ in the carbonization.

![Graph](image)

Fig. 2. Variations of H₂ flow rate with carbonization time.

![Graph](image)

Fig. 3. Variations of CO flow rate with carbonization time.
Fig. 4. Variations of CO$_2$ flow rate with carbonization time in the carbonization.

Fig. 5. Total gas volume generated by the carbonization of coal as a function of $T_{C, \text{max}}$.

Maximum carbonization temperature $T_{C, \text{max}}$ (K)

3.2 Effect of residual volatile matter on reduction

In order to investigate the effect of V.M. on reduction, carbon composite iron oxide pellets bearing the semi-coal-char at $T_{C, \text{max}} = 823, 873, 973, 1073$ and $1273$ K were heated from room temperature to $T_{R, \text{max}} = 1273$ K at 3 K min$^{-1}$ in the nitrogen gas atmosphere. Then, the reduced pellets were analyzed by XRD. The XRD pattern of the sample at $T_{C, \text{max}} = 823$ K before reduction is depicted in Fig. 6. The sample is identified as hematite (Fe$_2$O$_3$), carbon (char) and Bentonite. The weak peak of 26$^\circ$~27$^\circ$ concerning carbon and Bentonite overlaps each other. Figure 7 shows the XRD patterns of the samples after reduction. In all samples, the peaks of Fe are confirmed. Furthermore, the peak of Fe is found to be stronger at the lower $T_{C, \text{max}}$. The peak of Fe$_2$O$_3$ in the reduced samples is not observed. This indicated that the reduction rate of the sample obtained at $T_{C, \text{max}} = 823$ K was faster than any other samples. On the other hand, in all samples, carbon direct reaction had a little influence on iron oxide reduction because $T_{R, \text{max}}$ was just reaching and not keeping at 1273 K. From these results, when $T_{C, \text{max}}$ was lower, namely the pellet had more V.M., the reduction of iron oxide was more accelerated. On the other hand, cracks in all samples after reduction were not observed. This result indicated that some strength of the pellets was kept by the addition of Bentonite.

Fig. 6. XRD pattern of a carbon composite pellet bearing the semi-coal-char obtained at $T_{C, \text{max}} = 823$ K before reduction.

Fig. 7. XRD patterns of carbon composite pellets bearing semi-coal-char obtained at $T_{C, \text{max}} = 823, 873, 973, 1073$ and $1273$ K after reduction from room temperature to $T_{R, \text{max}} = 1273$ K at 3 K/min.

Furthermore, carbon composite iron oxide pellet bearing the semi-coal-char obtained at $T_{C, \text{max}} = 823$ K was reduced from room temperature to $T_{R, \text{max}} = 873, 973, 1073, 1173$ and $1273$ K at 3 K min$^{-1}$ in the nitrogen gas atmosphere. The XRD patterns are shown in Fig. 8. These peaks of Fe$_2$O$_3$ are strong, but peaks of Fe$_3$O$_4$ are weak. The slight reduction from the original Fe$_2$O$_3$ to Fe$_3$O$_4$ was
caused by the V.M. in the semi-coal-char. The reduction of iron oxide was not still accelerated at $T_{R_{\text{max}}} = 873$ K. On the other hand, the existence of Fe$_2$O$_3$ is clearly seen in the sample obtained at $T_{R_{\text{max}}} = 973$ and 1073 K, which shows the original Fe$_2$O$_3$ was gradually reduced to Fe$_3$O$_4$. And in the XRD pattern of the sample obtained at $T_{R_{\text{max}}} = 1173$ K, the identified phases are Fe, FeO and Fe$_2$O$_4$, where the peak of FeO is strong. From this result, the reduction of iron oxide was accelerated considerably from 1073 K to 1173 K. Here, it was considered that the solid-solid reaction between iron oxide and char started at lower temperature than normal solid-solid reaction over 1273 K. This lower sintering temperature was caused by the reactive semi-coal-char with residual V.M. Finally, the original Fe$_2$O$_3$ was almost reduced to Fe at $T_{R_{\text{max}}} = 1273$ K.

![Fig. 8. XRD patterns of carbon composite pellets bearing the semi-coal-char obtained at $T_{R_{\text{max}}} = 823$ K after reduction from room temperature to $T_{R_{\text{max}}} = 873$, 973, 1073, 1173 and 1273 K at 3 K/min.](image)

After the reduction, the morphology of carbon composite pellet was investigated. Cross sectional SEM images of reduced pellets at $T_{R_{\text{max}}} = 873$, 1073, 1273 K are shown in Figs. 9, 10, 11, respectively. In the reduced pellets at $T_{R_{\text{max}}} = 873$ K, black dots of char were observed. These dots of char were not reacted with iron oxides yet. Reduced pellets at $T_{R_{\text{max}}} = 1073$ K have some pores under 100 μm. These pores are produced by reaction of char during reduction of iron oxide. In the reduced pellet at $T_{R_{\text{max}}} = 1273$ K, residual char decreased clearly and a few pore with a size of 200 μm appeared. From these results, the less char existed, the larger pore increased.

On the other hand, in order to investigate the fractional reduction, carbon composite iron oxide pellet bearing the semi-coal-char obtained at $T_{C_{\text{max}}} = 823$, 1073 and 1273 K was reduced at $T_R = 1073$ and 1173 K in the nitrogen gas atmosphere. The relation between fractional reduction and reduction time of carbon composite pellets at 1073 K is shown in Fig. 12. Fractional reduction of carbon composite pellets at $T_{C_{\text{max}}} = 823$ K was higher than any other pellets by about 10%. Figure 13 shows the relation between fractional reduction and reduction time of carbon composite pellets at 1173 K. Fractional reduction of carbon composite pellets at $T_{C_{\text{max}}} = 823$ K was also higher than any other pellets by about 10%. This result was similar to the result obtained at 1073 K. From these results, when $T_{C_{\text{max}}}$ was lower, namely the pellet had more residual V.M., the reduction of iron oxide was much enhanced.

![Fig. 9. Cross sectional SEM image of reduced pellet at $T_{C_{\text{max}}} = 823$ K after reduction from room temperature to $T_{R_{\text{max}}} = 873$ K at 3 K/min.](image)

![Fig. 10. Cross sectional SEM image of reduced pellet at $T_{C_{\text{max}}} = 823$ K after reduction from room temperature to $T_{R_{\text{max}}} = 1073$ K at 3 K/min.](image)

![Fig. 11. Cross sectional SEM image of reduced pellet at $T_{C_{\text{max}}} = 823$ K after reduction from room temperature to $T_{R_{\text{max}}} = 1273$ K at 3 K/min.](image)
Fig. 12. Relationship between fractional reduction and reduction time of carbon composite pellets at 1073 K.

Fig. 13. Relationship between fractional reduction and reduction time of carbon composite pellets at 1173 K.

In consideration of these, the effect of residual V.M. on reduction of iron oxide in carbon composite pellets was clarified. These effects lead to novel iron ore agglomerates.

4. Conclusions
Carbon composite iron oxide pellets bearing the semi-coal-char with residual V.M. have been prepared and the effect of V.M. on reduction was evaluated. The results obtained are summarized as follows:
(1) The semi-coal-char obtained at $T_{C,max} = 823$ K retained much V.M. Most of V.M. was $H_2$.
(2) When $T_{C,max}$ was lower, namely the pellet had more residual V.M., the reduction of iron oxide was more accelerated.
(3) The original $Fe_2O_3$ in the pellet bearing the semi-coal-char obtained at $T_{C,max} = 823$ K was mainly reduced to $Fe_2O_3$ at $T_{R,max} = 973$ K and 1073 K, to $FeO$ at $T_{R,max} = 1173$ K and to Fe at $T_{R,max} = 1273$ K.

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References