INFLUENCE OF RESIDUAL VOLATILE MATTER IN CHAR ON REDUCTION OF IRON OXIDE IN CARBON COMPOSITE PELLETS [1]

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Abstract

Newcastle blend coal were carbonized partly at maximum carbonization temperatures ($T_{C,\ max}$ = 823～1273 K) in order to obtain semi-coal-char with residual volatile matter (V.M.). Carbon composite pellets using such semi-coal-char were reduced (at reduction temperature T_R = 1073, 1173, 1273 and 1373 K) in N_2 gas atmosphere. Fractional reduction *F*(%) of the carbon composite pellet at $T_{C,\ max}$ = 823 K was 24 % for 60 min at T_R = 1073 and and over 60 % for 90 min at T_R = 1173 K. The pellet at $T_{C,\ max}$ = 823 K was reduced higher than any other pellets by about 10 % at T_R = 1073 an 1173 K. When $T_{C,\ max}$ was lower, namely the pellet had more residual V.M., the reduction of iron oxide was more accelerated at T_R = 1073 and 1173 K. Fractional reductions *F*(%) of the carbon composite pellets at $T_{C,\ max}$ = 823, 1073 and 1273 K were about 100 % for 60 min at T_R = 1273 K and for 30 min at T_R = 1373 K. These reducibilities of the carbon composite pellets were not dependent on residual V.M. over 1273 K.

Key words: Ironmaking; Volatile matter; Char; Carbon composite pellet.

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1 INTRODUCTION

In recent years, a lot of works have been reported on carbon composite iron ore agglomerates.[1-3] 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, these 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, carbon composite iron ore agglomerates are focused on utilizing as raw materials for 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, $T_{C,\ max}$, semi-coal-char with residual volatile matter (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.[12] 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 $T_{C,\ max}$ under a rising temperature condition. In this work, carbon composite iron oxide pellets using the above-mentioned semi-coal-char have been prepared and the influence of residual V.M. on reduction was evaluated.

2 EXPERIMENTAL

2.1 Sample

Newcastle blend coal (Fixed carbon: 53.4 mass%, V.M.: 41.3 mass%, Ash: 5.3 mass%) as a coal sample and reagent grade hematite Fe_2O_3 (95 mass%, Wako Pure Chemical Industries, Ltd.) as an iron oxide sample were used. The Newcastle blend coal had much V.M. of 41.3 mass%. Carbonization of coal under rising temperature conditions was interrupted at certain temperatures, $T_{C,\ max}$ = 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 Fe_2O_3 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 range of the mixture was regulated as 45～63 μm by the sieves. Finally, the proposed carbon composite iron oxide pellets bearing residual volatile matter were prepared by hand rolling.

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 draw of experimental apparatus is shown in Figure 1. The coal particles were packed in the carbonization reactor. N_2 gas was entered from the top of the reactor, which was heated at 200 K h^{-1} by a digital thermo-controller. N_2 gas with a constant flow rate of 1.67×10^{-5} (m^3 s^{-1} (s.t.p.)) was passed through the coal-packed bed and mixed with the carbonizing gas to determinate each gas flow rate.[13] This outlet gas mixture was filtered through glass wool to remove the tar. The resultant 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).

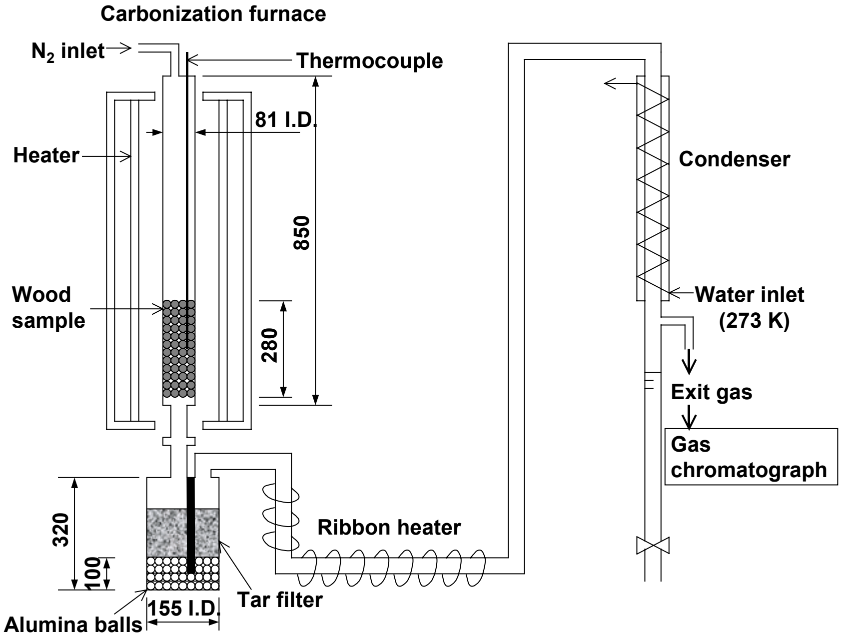

Figure 1. A schematic view of experimental apparatus for carbonization; dimensions in mm.

2.3 Reduction of Iron Oxide

Carbon composite iron oxide pellets using semi-coal-char were kept at 373 K for 24 h in the air in order to remove water. These carbon composite pellets were reduced isothermally at T_R = 1073, 1173 and 1273 K in N_2 gas atmosphere. Moreover, these formed pellets were heated from room temperature to maximum reduction temperatures, $T_{R,\ max}$ = 873, 973, 1073, 1173 and 1273 K at a heating rate of 3 K min^{-1} in N_2 gas atmosphere in order to investigate the influence of residual V.M. on reduction precisely. After reduction, obtanied pellets were analyzed by XRD (RINT2500V, Rigaku Corporation) with CuKα line at 40 kV and 200 mA and SEM (JEOL 5600, JEOL Ltd.).

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 $T_{C,\ max}$ = 823, 873, 973, 1073 and 1273 K at 200 K h^{-1}, and kept at $T_{C,\ max}$ until arrival time of 6 h. Total gas volumes of gas components generated by carbonization are calculated by integrating these gas flow rates, and are shown in Figure 2. H_2 gas is released more than any other gas under all the conditions except for $T_{C,\ max}$ = 823 K. The higher $T_{C,\ max}$ is, the more H_2 gas is released. But, H_2 gas volume is less than the other gas volume at $T_{C,\ max}$ = 823 K. From this result, it was found that the char retained much V.M., namely H_2, at $T_{C,\ max}$ = 823 K. In consideration of these, the semi-coal-char with some residual V.M. could be prepared by controlling $T_{C,\ max}$ in the carbonization.

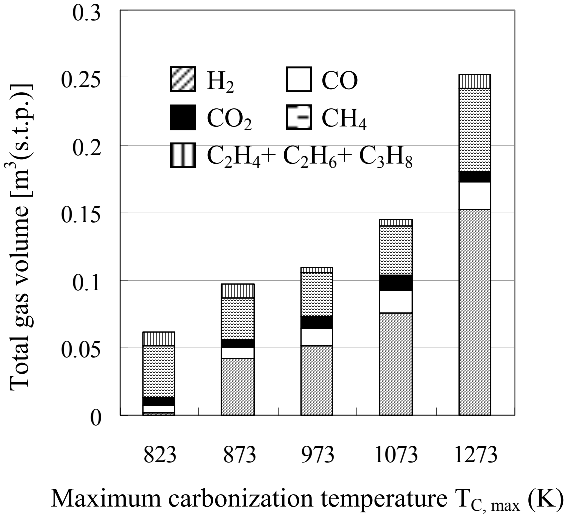

Figure 2. Total gas volume generated by the carbonization of coal as a function of $T_{C,\ max}$.

3.2 Influence of Residual Volatile Matter on Reduction

In order to investigate the fractional reduction *F*(%), carbon composite iron oxide pellets using semi-coal-char obtained at $T_{C,\ max}$ = 823, 1073 and 1273 K were reduced isothermally at T_R = 1073, 1173,1273 and 1373 K in N_2 gas atmosphere. The relationship between fractional reduction *F*(%) and reduction time at T_R = 1073 K is shown in Figure 3. Fractional reduction *F*(%) of the carbon composite pellet at $T_{C,\ max}$ = 823 K was 24 % for 60 min and was higher than any other pellets by about 10 %. Figure 4 shows the relationship between fractional reduction *F*(%) and reduction time at T_R = 1173 K. Fractional reduction *F*(%) of the carbon composite pellet at $T_{C,\ max}$ = 823 K was over 60 % for 90 min and was also higher than any other pellets by about 10 %. This result was similar to the result obtained at T_R = 1073 K. From these results, when $T_{C,\ max}$

was lower, namely the pellet had more residual V.M., the reduction of iron oxide was much enhanced at T_R = 1073 and 1173 K.

On the other hand, the relationships between fractional reduction *F*(%) and reduction time at T_R = 1273 and 1373 K are shown in Figures 5 and 6, respectively. Fractional reductions *F*(%) of carbon composite pellets at ($T_{C, max}$ = 823, 1073 and 1273 K) were about 100 % for 60 min and indicated similar behavior at T_R = 1273. Futhermore, fractional reductions *F*(%) of all carbon composite pellets reached about 100 % for 30 min at T_R = 1373. From these results, these reducibility of carbon composite pellets were high and were not dependent on residual V.M. over 1273 K.

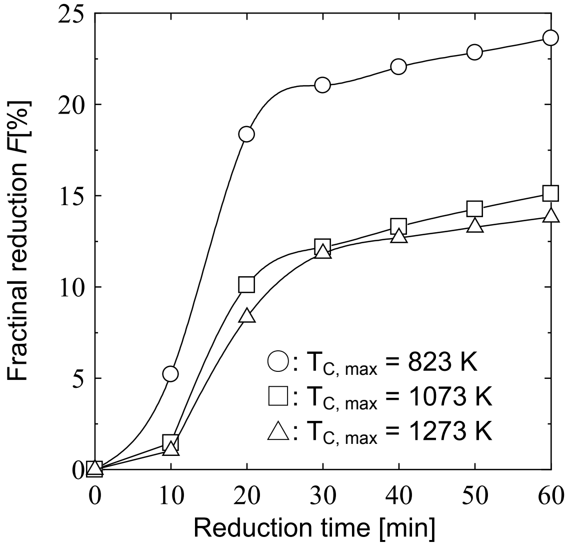

Figure 3. Reduction curves of carbon composite pellets at T_R = 1073 K in N_2 gas atmosphere.

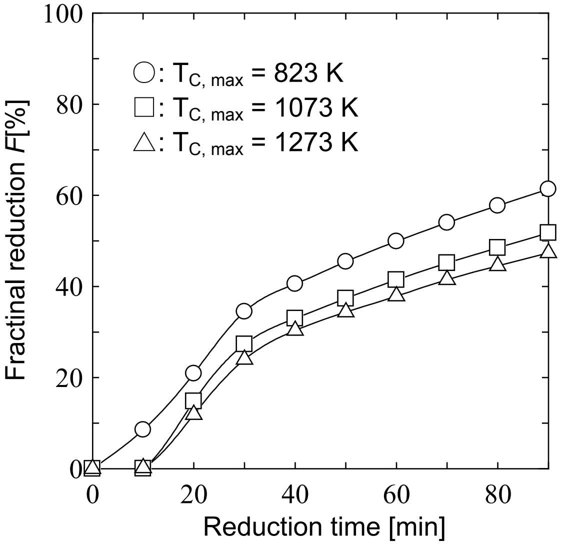

Figure 4. Reduction curves of carbon composite pellets at T_R = 1173 K in N_2 gas atmosphere.

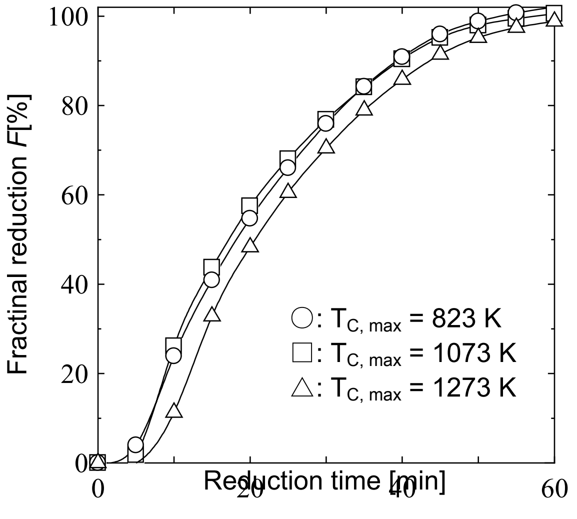

Figure 5. Reduction curves of carbon composite pellets at T_R = 1273 K in N_2 gas atmosphere.

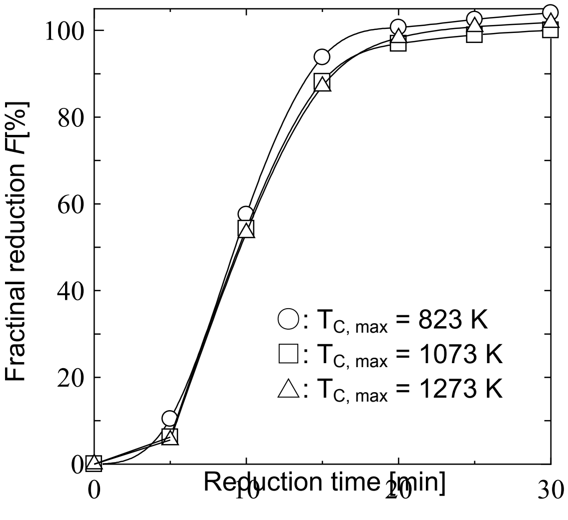

Figure 6. Reduction curves of carbon composite pellets at T_R = 1373 K in N_2 gas atmosphere.

After the reduction, the morphology of carbon composite pellet was investigated. Cross sectional SEM images of reduced pellets at T_R = 873, 1073, 1273 and 1373 K are shown in Figures 7, 8, 9 and 10, respectively. In the reduced pellets at T_R = 1073 K for 60 min, black dots of char were observed. These dots of char were not reacted with iron oxides yet. The reduced pellet at T_R = 1173 K for 90 min has a small amout of metallic Fe phase from the XRD and EPMA analyses. From this result, the hematite sample was partly changed to metallic Fe phase at T_R = 1173 K. Furthermore, reduced pellets at T_R = 1273 for 60 min and 1373 K for 30 min were covered with the metallic Fe phase and some pores appeared. These pores were produced by reaction of char during reduction of iron oxide and were smaller as T_R increased.

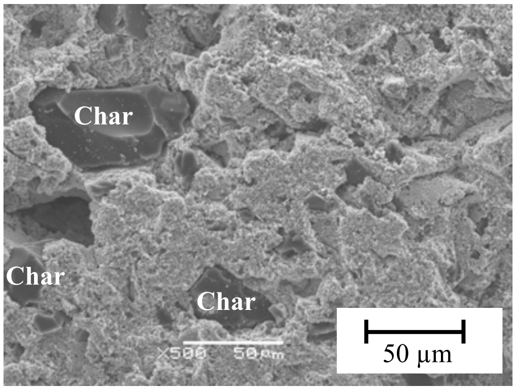

Figure 7. Cross sectional SEM image of carbon composite pellet containing char at $T_{C,\,max}$ = 823 K after reduction at T_R = 1073 K for 60 min in N_2 gas atmosphere.

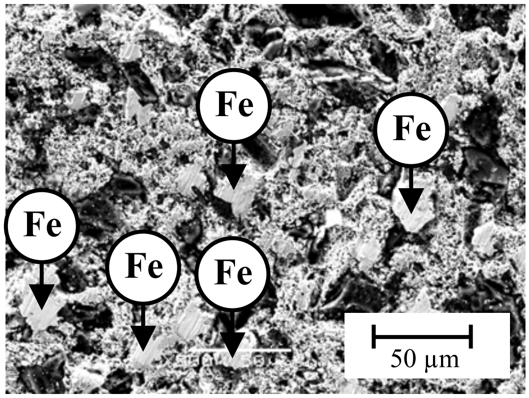

Figure 8. Cross sectional SEM image of carbon composite pellet containing char at $T_{C,\,max}$ = 823 K after reduction at T_R = 1173 K for 90 min in N_2 gas atmosphere.

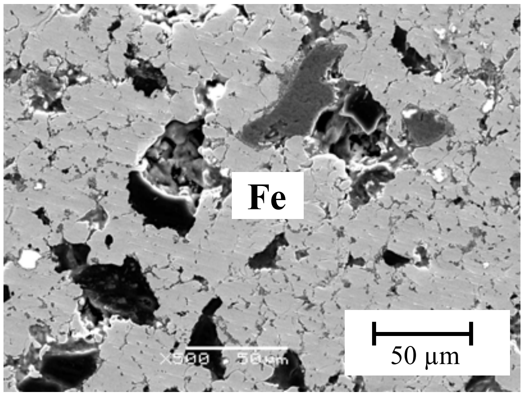

Figure 9. Cross sectional SEM image of carbon composite pellet containing char at $T_{C,\,max}$ = 823 K after reduction at T_R = 1273 K for 60 min in N_2 gas atmosphere.

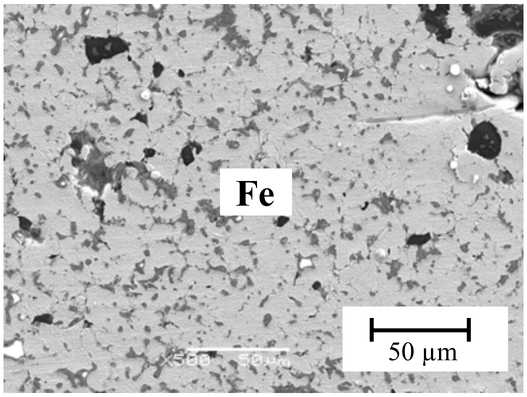

Figure 10. Cross sectional SEM image of carbon composite pellet containing char at $T_{C,\,max}$ = 823 K after reduction at T_R = 1373 K for 30 min in N_2 gas atmosphere.

Furthermore, carbon composite iron oxide pellet using the semi-coal-char obtained at $T_{C,\ max}$ = 823 K was reduced from room temperature to $T_{R,\ max}$ = 873, 973, 1073, 1173 and 1273 K at 3 K min^{-1} in N_2 gas atmosphere. The XRD pattern of the sample at $T_{C,\ max}$ = 823 K before reduction is depicted in Figure 11. The sample is identified as hematite (Fe_2O_3), carbon (char) and Bentonite. The weak peak of 26～27° concerning carbon and Bentonite overlaps each other. Figure 12 shows XRD patterns of samples after reduction. Peaks of Fe_2O_3 are strong, but peaks of Fe_3O_4 are weak at $T_{R,\ max}$ = 873 K. The slight reduction from Fe_2O_3 to Fe_3O_4 is thought to be caused by the residual V.M. in the semi-coal-char. The reduction of iron oxide was not accelerated at $T_{R,\ max}$ = 873 K. On the other hand, the existence of Fe_3O_4 is clearly seen in the sample obtained at $T_{R,\ max}$ = 973 and 1073 K, which shows the original Fe_2O_3 was gradually reduced to Fe_3O_4. And in the XRD pattern of the sample obtained at $T_{R,\ max}$ = 1173 K, the identified phases are Fe_3O_4 and FeO, where the peak of FeO is strong. From this result, the reduction of iron oxide was accelerated considerably at $T_{R,\ max}$ = 1173 K. Here, it was considered that the reduction between iron oxide and semi-coal-char started at lower temperature than the normal reduction between iron oxide and coke. This lower starting temperature was caused by the reactive semi-coal-char with residual V.M. Finally, the original Fe_2O_3 was almost reduced to Fe at $T_{R,\ max}$ = 1273 K.

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

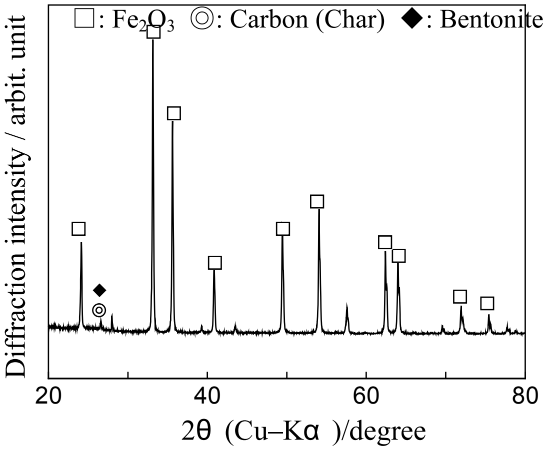

Figure 11. XRD pattern of the carbon composite pellet using the semi-coal-char obtained at $T_{C,\ max}$ = 823 K before reduction.

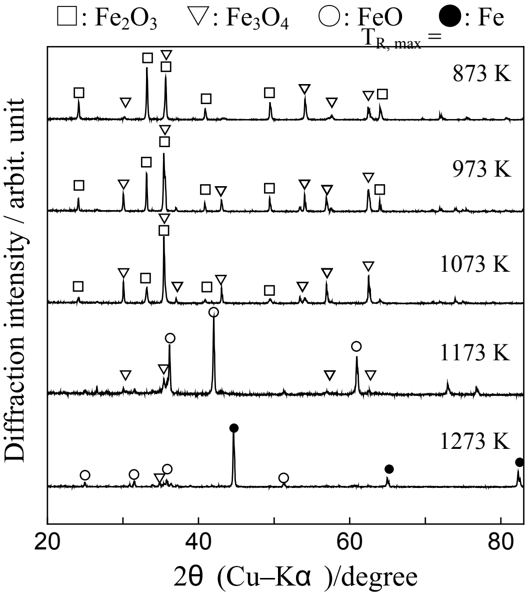

Figure 12. XRD patterns of carbon composite pellets using semi-coal-char obtained at $T_{C,\ max}$ = 823 K after reduction from room temperature to $T_{R,\ max}$ = 873, 973, 1073, 1173 and 1273 K at 3 K/min.

4 CONCLUSIONS

Carbon composite iron oxide pellets using the semi-coal-char with residual V.M. have been prepared and the influence of residual V.M. on the reduction rate was evaluated in N_2 gas atmosphere. 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) Fractional reduction *F* of carbon composite pellet at $T_{C, max}$ = 823 K was 24 % for 60 min and was higher than any other pellets by about 10 % at T_R = 1073 K.
(3) Fractional reduction *F* of carbon composite pellet at $T_{C, max}$ = 823 K was over 60 % for 90 min and was higher than any other pellets by about 10 % at T_R = 1173 K.
(4) When $T_{C, max}$ was lower, namely the pellet had more residual V.M., the reduction of iron oxide was more accelerated at T_R = 1073 and 1173 K.
(5) Fractional reductions *F* of carbon composite pellets at $T_{C, max}$ = 823, 1073 and 1273 K were about 100 % for 60 min at T_R = 1273 K and for 30 min at T_R = 1373 K, respectively. Such reducibility of carbon composite pellets was high and was not dependent on residual V.M. over 1273 K.
(6) 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_3O_4 at $T_{R, max}$ = 973 and 1073 K, to FeO at $T_{R, max}$ = 1173 K and to Fe at $T_{R, max}$ = 1273 K.

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