The Characteristics of Catalyst-coated Highly Reactive Coke

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It is important to develop the production and utilization technology of highly reactive coke in order to improve the efficiency of blast furnace reactions. In this study, the characteristics of catalyst-coated highly reactive coke produced by the ‘post-addition of catalyst to coke’ method were investigated. First, the catalytic effect of Fe and Ca on graphite and deashed coke during the C–CO$_2$ reaction was investigated. Fe and Ca addition increased the reaction rate and decreased the reaction beginning temperature. Second, the reaction rate of Fe or Ca coated coke was kept high until the weight loss reached 10%. This means that a high catalytic effect is maintained in the thermal reserve zone of the blast furnace. Furthermore, it was found that 70% of the catalyst coated on the coke surface remains after drop impacts. It is expected that the loss of catalyst during coke handling and transportation is small. Catalyst-coated highly reactive coke is promising for improving the efficiency of blast furnace reactions.

KEY WORDS: coke reactivity; catalyst; ironmaking; cokemaking; reaction efficiency; blast furnace; thermal reserve zone.

1. Introduction

Improvement in the efficiency of blast furnace reactions during the blast furnace ironmaking process is important since it has the potential to allow a decrease in the reducing agent rate (the amount (in kg) of reducing agents such as coke and coal needed to produce 1 000 kg of pig iron) as well as CO$_2$ emissions. Naito et al.1,2) proposed a technology that dramatically improves the reaction efficiency in blast furnaces by decreasing the temperature of the thermal reserve zone through the use of highly reactive coke. Here the reactivity of coke refers to the reaction rate of coke with CO$_2$ (solution loss reaction C+$\text{CO}_2$=2CO). The use of highly reactive ‘nut’ coke in a commercial scale blast furnace is reported to improve the reaction efficiency3) and decrease the temperature of the thermal reserve zone through the use of highly reactive coke. Here the reactivity of coke refers to the reaction rate of coke with CO$_2$ (solution loss reaction C+$\text{CO}_2$=2CO). The use of highly reactive ‘nut’ coke in a commercial scale blast furnace is reported to improve the reaction efficiency3) and decrease the temperature of the thermal reserve zone.4) However, no practical methods have been devised to produce the nut coke with high reactivity and strength. Therefore, we investigated methods to produce highly reactive coke with high strength that can be used in an actual blast furnace, by utilizing the catalytic effect.

There have been many studies on the catalysts for CO$_2$ gasification of coal and char.5–9) The effect of ash on CO$_2$ gasification,10) the order of catalytic activity and the mechanism of catalytic reaction of the alkaline metals such as Na and K,11–13) Li,14) the alkaline earth metals15) such as Ca and Ba,16) the transition metals such as Fe,17,18,19) Ni20) have been thoroughly and extensively studied. On the other hand, there are relatively few quantitative data concerning the reactivity of blast furnace coke containing these catalysts in the condition of the thermal reserve zone in a blast furnace, i.e. relatively low temperature (approximately 1 000°C), CO$_2$/CO mixture, low weight loss (at most 20%).

There are two basic methods of adding the catalyst to the coke21); (1) the ‘post-addition of catalyst to coke’ method, where the catalyst and/or catalyst solution is sprayed onto the coke after the coke is pushed out of the coke oven chamber, and (2) the ‘pre-addition of catalyst to coke’ method, where the catalyst is mixed with coal before the mixture is carbonized in the coke oven chamber. Adjustment of the ash components through coal selection is involved in the latter method. First we investigated the latter method (2) and found that strong, highly reactive ‘lump’ coke could be produced in commercial scale coke ovens by adding a Ca-rich coal and adjusting the coal blend composition. Use of the Ca-rich coke in Muroran No. 2 Blast Furnace for a long period caused a decrease in the reducing agent rate.21) On the other hand, in the ‘pre-addition of catalyst to coke’ method, there are other factors to take into account such as (a) deterioration of the coke strength by carbonizing coal and catalyst (inert substances) together and (b) changes in the elements in charged material and an increase in slag volume by adding excess catalyst to the interior of the coke.

The ‘post-addition of catalyst to coke’ method, where catalysts are added after carbonization, does not affect the coke strength. On the other hand, there is concern that the catalytic effect might disappear or weaken as the reaction layer moves toward the inner part of the coke since catalysts...
are coated on the surface of the coke. There have been few studies on this subject. Even a decrease in the catalytic activity itself during reaction has been reported.\textsuperscript{22)} Furthermore, there is another concern that the catalyst coated on the coke might be separated during the handling process of the coke (mechanical impacts through transportation and drops), however, there have been few studies on this subject.

Therefore in this report, first we investigated the effect of catalyst-coating on the reactivity and the reaction beginning temperature of blast furnace coke in an atmosphere closely resembling that of the thermal reserve zone in a blast furnace. Second, we studied the durability of the catalytic effect of the catalyst coated on the coke surface and third we investigated the separation of the catalyst coated on coke by mechanical impacts.

2. Experimental

2.1. Evaluation of the Reactivity of Catalyst-coated Blast Furnace Coke

Blast furnace coke is heterogeneous carbon that contains a large amount of impurities (ash). Therefore, first, graphite was used to evaluate the effect of catalyst on the reaction of pure carbon and CO\textsubscript{2}. Second, deashed coke was used as a pure-carbon like material to investigate the dependence of catalytic activity on carbon structure. Third, deashed coke and untreated coke (that is blast furnace coke) were compared in order to investigate the effect of ash on the catalytic activity.

2.1.1. Catalyst Coating on Graphite

First, the catalytic effect during graphite–CO\textsubscript{2} reaction was investigated. High purity graphite (TIMREX KS150-600SP, Ash<0.5\%, 150–300 μm) was used in this experiment. All the catalyst solution with a desired concentration was added on to 10 g of graphite. Then the sample was mixed with a spatula and dried at 120°C for over 12 h. Next, the catalyst left in the container sidewall was washed with a small amount of water and mixed with graphite again. Then the sample was dried again. In order to obtain the amount of the catalyst added to the graphite, M (metal element in the mixed sample) and C was analyzed quantitatively and the molar ratio of M/C was calculated. M was analyzed by ICP (Inductively Coupled Plasma) and C was analyzed by the combustion infrared absorption technique.

Fe and Ca were investigated as catalyst. [Fe(NO\textsubscript{3})\textsubscript{2}·9H\textsubscript{2}O] (Kanto Chemical Co.) was used to add Fe to graphite so that the molar ratio of Fe/C would become 0.02, 0.002 and 0.0002. Ca(NO\textsubscript{3})\textsubscript{2} (Kanto Chemical Co.) was used to add Ca to graphite so that the atomic ratio of Ca/C would become 0.002. The measured amount of the catalyst coated on graphite was shown in Table 1. It is clear that the measured value is close to the calculated value.

2.1.2. Catalyst Coating on Deashed Coke and Untreated Coke

In the next step, the catalyst was added to a deashed coke and an untreated coke. In this report, the deashed coke refers to the coke carbonized from Deashed Coal A and the untreated coke refers to the coke carbonized from Untreated Coal A. Deashed Coal A and Untreated Coal A (Table 2, –150 μm) were dried and heated to 900°C at 10°C min\textsuperscript{-1} in a tubular infra-red furnace in a nitrogen atmosphere (2 NL min\textsuperscript{-1}), then kept for 5 min to obtain the coke sample. The coke sample was crushed to –300 μm and Fe solution was added on to 10 g of the coke sample in the same way as in Fe coating on graphite.

Deashing of coal was carried out according to the following procedure used by Samaras\textsuperscript{23)}

\begin{itemize}
  \item (1) 20 g of coal (–150 μm) and 200 cc of 5 N HCl (aq.) (doublefold diluted solution of concentrated hydrochloric acid) was placed in a 300 cc beaker made of polyethylene and mixed at 60°C for 1 h. Then it was filtrated and washed with hot distilled water.
  \item (2) The solid residue was mixed with 200 cc of 22 N HF at 60°C for 1 h and then filtrated and washed.
  \item (3) The solid residue was mixed with 200 cc of 10 N HCl (aq.) at 60°C for 1 h and then filtrated and washed.
\end{itemize}

2.1.3. Evaluation of Reactivity Using Thermobalance

In order to investigate the catalytic effect on graphite and deashed/untreated coke, the weight loss during the C–CO\textsubscript{2} reaction was measured using TGA (thermogravimetric analysis). The instrument used was a Shimazu TG-50. Approximately 20 mg of the sample was inserted into the sample cell of the TGA and heated from room temperature to 1000°C in a reaction gas atmosphere, at a heating rate of 10°C min\textsuperscript{-1}. The standard reaction gas composition was CO\textsubscript{2}/CO=100/0. In addition to this, in the case of Fe-coated graphite the reaction gas of CO\textsubscript{2}/CO=98.5/1.5, 90/10, 50/50 and 20/80 was used and in the case of Ca-coated graphite the reaction gas of CO\textsubscript{2}/CO=50/50 was used. The gas flow rate was 50 cm\textsuperscript{3} min\textsuperscript{-1}. Here the reaction beginning temperature was defined as the lowest temperature where the weight loss rate always exceeds 0.00025 min\textsuperscript{-1}.

### Table 1. The measured amount of the catalyst coated on graphite.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Metal/C (mol/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>target measured</td>
</tr>
<tr>
<td>Fe</td>
<td>0.02  0.016</td>
</tr>
<tr>
<td>Fe</td>
<td>0.002  0.0002</td>
</tr>
<tr>
<td>Fe</td>
<td>0.0002  0.00025</td>
</tr>
<tr>
<td>Ca</td>
<td>0.002  0.0020</td>
</tr>
</tbody>
</table>

### Table 2. Characterization data for the coals used.

<table>
<thead>
<tr>
<th>Coal</th>
<th>Proximate analysis (mass % db)</th>
<th>Total ash (vol. %)</th>
<th>Maximum fluidity (log MF/dspm)</th>
<th>Mean reflectance (%)</th>
<th>Major ash component (mass %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>23.5  8.6</td>
<td>91</td>
<td>2.78</td>
<td>1.21</td>
<td>P\textsubscript{2}O\textsubscript{5} K\textsubscript{2}O Na\textsubscript{2}O SiO\textsubscript{2} Al\textsubscript{2}O\textsubscript{3} Fe\textsubscript{2}O\textsubscript{3} CaO MgO</td>
</tr>
<tr>
<td>B</td>
<td>24.0  9.9</td>
<td>104</td>
<td>2.94</td>
<td>1.18</td>
<td>0.45  0.93  0.70  59.29  30.40 3.49  0.62  0.46</td>
</tr>
<tr>
<td>C</td>
<td>35.5  9.4</td>
<td>30</td>
<td>2.17</td>
<td>0.75</td>
<td>0.42  1.03  0.62 161.97 24.80 5.10 1.58 0.83</td>
</tr>
</tbody>
</table>
2.2. Evaluation of the Reactivity of Catalyst-coated Coke and the Durability of the Catalytic Effect

In the next step, catalysts were coated on cylindrical coke samples by the 'post-addition of catalyst to coke' method and their reactivity was investigated using the TGA in the atmosphere closely resembling that of the thermal reserve zone in a blast furnace. In addition to the TGA analysis, as an industrial method to evaluate the coke reactivity, the JIS coke reactivity index (JIS R,I) of the catalyst-coated coke and CRI of the catalyst-coated nut coke were also examined. Furthermore, the durability of the catalytic effect for catalyst-coated cylindrical coke and nut coke were investigated.

2.2.1. Catalyst Coating on Cylindrical Coke Samples

In this experiment, a cylindrical coke sample (of diameter 10 mm, length 15 mm) was used since the sample needs to be both sufficiently large to be treated with the catalyst coating procedure described below and sufficiently small to be analyzed by the TGA. First, Coals B and C (Table 2) were crushed to 80% <3 mm and a blended coal was then prepared by mixing Coals B and C (Coal B 70%, Coal C 30%). The sample was charged in a steel box (420 mm wide, 600 mm long and 400 mm high) at a bulk density of 830 dry-kg m$^{-3}$. The box was then placed in an electrically heated test oven and carbonized for 18.5 h under heating conditions equivalent to the flue temperature of 1250°C in an actual coke oven$^{24}$ and quenched with nitrogen. DI$^{15,25}$ for the resultant coke was 81.3, CRI$^{26}$ was 25.6 and JIS R,I$^{25}$ was 14.4 respectively. Cylindrical coke samples were cut out of the body part (in the middle of the oven wall and center) of the resultant lump coke.

Furthermore, various catalysts ($\text{CaCl}_2, \text{CaCO}_3, \text{CaO}, \text{Fe(NO}_3)_3$) were used to prepare 0.2–1.0 Ca-mol/L (0.8–4.0 mass% Ca) and 0.02–1.0 Fe-mol/L (0.11–5.5 mass% Fe) aqueous solution. The cylindrical coke samples were dipped in the solution for 5 min and used for the following reactivity tests after drying.

2.2.2. Evaluation of the Reactivity of Catalyst-coated Coke Using the Macro-TGA

The instrument (macro-TGA) used was a Shimazu TGA51H. The sample on a Mo cell was placed in the TGA and heated from room temperature to the desired reaction temperature (1 050, 1 100, 1 150°C) in a nitrogen atmosphere, at a heating rate of 50°C min$^{-1}$. The temperature was then maintained and the gas was changed to a reaction gas. The reaction gas composition was CO$_2$/CO in the container for 5 min. The sample was dried, sieved with a 0.5-mm sieve and then the JIS coke reactivity index was measured. Moreover approximately 200 g of the 20 mm nut coke for the Tests 2 and 3 was put into a 2 000 cc container with a lid and after mixing the sample and the catalyst solution for 5 min by shaking the container, the sample was taken out. A certain amount of the 20 mm nut coke for Tests 4 and 5 was put into a 10-liter container and taken out after mixing the sample and the catalyst solution in the container for 5 min. The sample was dried and then the CRI was measured.

2.2.4. JIS Coke Reactivity Index and CRI

The effect of catalyst coating on the coke reactivity indices used in steel industries was investigated. The JIS coke reactivity index (JIS R,I)$^{25}$ which stands for the chemical reaction rate of coke with CO$_2$ at a low temperature range, was measured as a means of evaluating the chemical reactivity of catalyst-coated coke breeze. In this method, 10 g of 0.85–1.7 mm coke breeze was reacted with CO$_2$, at 950°C and JIS R,I is calculated by $\text{CO}/(\text{CO}+2\text{CO}_2) \times 100\%$, where CO(%) is the concentration of CO at the outlet of the reactor and $\text{CO}_2(%)=100-\text{CO}(\%)$. Moreover, the CRI (Coke Reactivity Index: the percentage of weight loss to the original coke mass after reaction under $\text{CO}_2$ at 1 100°C for 2 h)$^{26}$ were measured for the catalyst-coated nut coke.

<table>
<thead>
<tr>
<th>Test</th>
<th>Dissolved or dispersed substance</th>
<th>Concentration</th>
<th>Dipping period (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>No addition</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>$\text{CaCl}_2$</td>
<td>1.0 mol-Ca/l</td>
<td>5 min</td>
</tr>
<tr>
<td>3</td>
<td>$\text{CaO}$ powder</td>
<td>10%</td>
<td>5 min</td>
</tr>
<tr>
<td></td>
<td>(1.6 mol-Ca/l)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>$\text{Fe(NO}_3)_3$</td>
<td>0.2 mol-Fe/l</td>
<td>5 min</td>
</tr>
<tr>
<td>5</td>
<td>$\text{Fe dust}$</td>
<td>10%</td>
<td>5 min</td>
</tr>
<tr>
<td></td>
<td>(1.0 mol-Fe/l)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 3. Experimental condition of the catalyst coating to coke.

<table>
<thead>
<tr>
<th>Component (mass %)</th>
<th>mean size (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>T-Fe</td>
<td>-</td>
</tr>
<tr>
<td>FeO</td>
<td>-</td>
</tr>
<tr>
<td>$P_2O_5$</td>
<td>-</td>
</tr>
<tr>
<td>$K_2O$</td>
<td>-</td>
</tr>
<tr>
<td>$Na_2O$</td>
<td>-</td>
</tr>
<tr>
<td>SiO$_2$</td>
<td>-</td>
</tr>
<tr>
<td>$Al_2O_3$</td>
<td>-</td>
</tr>
<tr>
<td>Fe$_2O_3$</td>
<td>-</td>
</tr>
<tr>
<td>CaO</td>
<td>-</td>
</tr>
<tr>
<td>MgO</td>
<td>-</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>-</td>
</tr>
<tr>
<td>MnO</td>
<td>-</td>
</tr>
<tr>
<td>SO$_2$</td>
<td>-</td>
</tr>
</tbody>
</table>

2.2.3. Catalyst Coating on Coke Breeze and Nut Coke

The experimental conditions are shown in Table 3. $\text{CaCl}_2$ aqueous solution, the water slurry of fine CaO powder and $\text{Fe(NO}_3)_3$ aqueous solution were used in Tests 2, 3 and 4 respectively. In Test 5 Fe dust slurry was diluted to a given concentration. Chemical compositions and mean particle size of CaO powder and Fe dust are shown in Table 4. The mean particle size was measured using the Laser Diffraction Particle Size Analyzer (Shimazu, SALD-3000FS).

Considering the catalyst coating to coke at the position near a blast furnace, the nut coke stabilized through CDQ, a coke cutter, a sieving plant and a transportation procedure was collected at a commercial plant. Two types of samples, i.e. (1) coke breeze (0.85–1.7 mm coke breeze for the JIS coke reactivity index test) and (2) 20 mm nut coke (20±1 mm nut coke for the CRI test) were prepared from the collected coke sample. Approximately 30 g of the coke breeze was put into a 100 cc beaker and after mixing the sample and the catalyst solution in the beaker for 5 min with a glass stick, the sample was taken out. The sample was dried, sieved with a 0.5-mm sieve and then the JIS coke reactivity index was measured. Moreover approximately 200 g of the 20 mm nut coke for the Tests 2 and 3 was put into a 2 000 cc container with a lid and after mixing the sample and the catalyst solution for 5 min by shaking the container, the sample was taken out. A certain amount of the 20 mm nut coke for Tests 4 and 5 was put into a 10-liter container and taken out after mixing the sample and the catalyst solution in the container for 5 min. The sample was dried and then the CRI was measured.

Table 4. Ash component and mean size of CaO powder and Fe dust.

<table>
<thead>
<tr>
<th>Component (mass %)</th>
<th>mean size (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaO powder</td>
<td>4.1 0.655 0.04 0.021 6.2 2.1 - 8.6 1.3 0.3 0.018 15</td>
</tr>
<tr>
<td>Fe dust</td>
<td>56.4 4.1 0.655 0.04 0.021 6.2 2.1 - 8.6 1.3 0.3 0.018 15</td>
</tr>
</tbody>
</table>
2.2.5. Evaluation of the Reactivity of Catalyst-coated Nut Coke Using the Large-scale Thermobalance

The instrument used was the large-scale thermobalance. The reaction gas is inserted into the reactor from the bottom and the weight loss can be monitored continuously by measuring the total weight of the reactor and the sample with a balance. First, 200 g of catalyst-coated nut (20 mm) coke samples (Tests 1, 3 and 4 in Table 3) was placed in the retort and heated to 1 100°C in a nitrogen atmosphere. The temperature was then maintained and the gas was changed to a reaction gas. The reaction gas composition was CO2/CO/H2=50/50, which closely resembles that of the thermal reserve zone in a blast furnace. The changes in weight were recorded as a function of time.

2.2.6. Evaluation of the Dispersion of the Catalyst Coated on Coke

In order to evaluate the distribution of the catalyst coated on coke, the coke samples (Tests 3 and 4 in Table 3) before and after the large-scale thermobalance experiment were analyzed using the EPMA technique.

2.3. Evaluation of the Separation of the Catalyst Coated on Coke by Mechanical Impacts

Here, considering that the ‘post-addition of catalyst to coke’ method would be applied to a commercial plant by spraying catalyst solution on coke near the blast furnace, Fe dust sludge (Table 4, slurry concentration is 20%) was sprayed on to the 20 mm nut coke (the same sample as used in Sec. 2.2.3) and the separation of the catalyst by mechanical impacts was investigated. First, approximately 400 g of the catalyst-coated nut coke samples was dropped from a height of 2 m onto a steel plate 1, 3, 6 and 10 times and the breeze (H11002/4.75 mm) generated by drop impacts was collected. Then the catalyst residual ratio was obtained by measuring the mass and the ash content of the breeze. Furthermore, CRI and JIS Rei for the coke before and after drop impacts were measured.

3. Results and Discussion

3.1. The Effect of Catalyst-coating on the Reactivity of Blast Furnace Coke

3.1.1. The Reactivity of Catalyst-coated Graphite

(1) Fe-coated Graphite

Figure 1 shows the weight loss of Fe-coated graphite during the C–CO2 reaction in CO2/CO=100/0. While the weight loss at 1000°C for catalyst no-addition coke is approximately 0.3%, Fe-coated graphite show a dramatic weight loss at approximately 900°C and above, which implies the catalytic activity of Fe. Furthermore, the weight loss increases with increasing the amount of Fe coated on graphite (Fe/C). The reaction beginning temperature for Fe coated graphite was approximately 830°C regardless of the amount of the catalyst and decreased to a great extent compared with 910°C for catalyst no-addition coke.

Then, the effect of CO on the weight loss of Fe-coated graphite during the C–CO2 reaction was investigated. As shown in Fig. 2, in the case of Fe-coated graphite, the weight loss in CO2/CO=98.5/1.5–50/50 was larger than that in CO2/CO=100/0. The weight loss rate was remarkably high at 930–970°C in CO2/CO=98.5/1.5–90/10 and at 900–930°C in CO2/CO=50/50. On the other hand, the weight loss in CO2/CO=20/80 was smaller than that in CO2/CO=100/0. This is thought to be because the mode of occurrence of Fe changes dramatically depending on the atmosphere (CO2/CO) and the temperature during the C–CO2 reaction and so does the catalytic activity of Fe. Moreover, the weight loss tends to level off when it reaches 50–80% at 950–970°C in the case of Fe/C=0.002 and 0.016 in Fig. 1 and also in the case of CO2/CO=100/0, 98.5/1.5, 90/10 and 50/50 in Fig. 2. This is thought to be because as the reaction proceeds, the amount of residual carbon decreases and the agglomeration of Fe is promoted, which leads to a sudden decrease in the carbon–Fe contact area and hence in the catalytic activity per unit mass of the catalyst. It is interesting that the catalytic activity of Fe during
the C–CO₂ reaction increases in the reaction gas composition including CO, which closely resembles that of the thermal reserve zone in a blast furnace.

(2) Ca-coated Graphite

Figure 3 shows the weight loss of Ca-coated graphite during the C–CO₂ reaction. Ca-coated graphite shows a dramatic weight loss at approximately 900°C and the reaction beginning temperature was 839°C in the case of CO₂/CO₁₀₀₀/H₁₁₀₀₁₀₀/0. On the other hand, the addition of CO to the reaction gas increases the reaction beginning temperature and decreases the reaction rate. This is thought to be because an increase in the concentration of CO inhibits the reduction of the carbonate by C (CaCO₃ → CaO + 2CO) in the CaO–CaCO₃ cycle model, which is proposed as the catalytic mechanism of Ca during the C–CO₂ reaction.

3.1.2. The Reactivity of Catalyst-coated Deashed Coke and Untreated Coke

(1) Ash Component of Coke

Table 5 shows the changes in ash component of coke by deashing and Fe-coating. Approximately 97.3% of ash was removed by the deashing process. The concentrations of Ca and Fe, which catalyze the C–CO₂ reaction, were 0.128% and 0.390% respectively before deashing and their effects are not negligible. They decreased to 30 ppm and 500 ppm after deashing. The concentrations of K and Na decreased from 200–500 ppm to below 5 ppm by deashing and their catalytic effects are relatively negligible after deashing. The amount of Fe coated on the deashed coke was 0.00103 mol-Fe/mol-C (equivalent to approximately 0.5 mass% Fe), calculated by the difference in the Fe contents in the coke before and after coating. The Fe contents in the untreated coke after Fe coating were calculated assuming that the amount of Fe coated on the untreated coke was the same as that coated on the deashed coke.

(2) Weight Loss of Catalyst-coated Deashed Coke and Untreated Coke

Figure 4 shows the effect of Fe-coating and deashing on the weight loss of coke (carbonized from Coal A) during the C–CO₂ reaction and Table 6 shows the changes in the reaction beginning temperature of coke by deashing and Fe-coating. Fe-coating decreased the reaction beginning temperature of the deashed coke by 135°C. The catalytic effect of ash in the deashed coke is almost negligible then this decrease in the reaction beginning temperature is explained by the catalytic effect of Fe as in the case of graphite.

Furthermore, Fe-coating decreased the reaction beginning temperature of the untreated coke by 88°C. The catalytic effect of Fe is thought to decrease the reaction beginning temperature of a normal blast furnace coke containing ash.

On the other hand, there is no remarkable difference between the weight losses of the untreated coke and the deashed coke. This was contrary to our expectations that the reactivity of the untreated coke would be higher than that of the deashed coke since the former contains more ash components, which are expected to act as catalysts. This is thought to be because deashing has two reverse effects on the C–CO₂ reaction: while it decreases the reactivity by removing catalytic ash components, it increases the reactivity by increasing the microporosity of the resultant coke. This subject requires further study.

Here, the heat treatment temperature of the coke is 900°C. Strictly speaking, in the thermobalance experiment over 900°C the weight loss caused by the pyrolysis of coke might be mixed. However, the reaction beginning temperature is below 900°C, which would not affect the interpretation of the results.

3.2. Evaluation of the Reactivity of Catalyst-coated Coke and the Durability of Catalytic Effect

3.2.1. Initial Reaction Rate of the Catalyst-coated Cylindrical Coke

First, we investigated the effects of the catalyst types, the concentration of the catalyst solution and the reaction temperature on the initial reaction rate of the catalyst-coated cylindrical coke. Figure 5 shows that Fe coating increases the reaction rate of the catalyst-coated cylindrical coke. Figure 6 shows the relationship between Fe concentration in coke and reaction rate at 1 100°C. Fe content in coke and the reaction rate increase with increasing the concentration of the Fe solution. Figure 7 shows that Ca coating increases the reaction rate of the catalyst-coated cylindrical coke irrespective of the types of the Ca salt. Figure 8 shows that the
reaction rate increases with increasing the Ca content in coke.

3.2.2. JIS Coke Reactivity Index of the Catalyst-coated Coke Breeze and CRI of the Catalyst-coated Nut Coke

Secondly, the effect of the ‘post-addition of catalyst to coke method’ on the reactivity indices used in steel industries (JIS coke reactivity index and CRI) was investigated. As shown in Figs. 9 and 10, the addition of Ca or Fe compounds increase the JIS coke reactivity index and CRI to a great extent. JIS coke reactivity index increased by 10–30 from 15.6 for the catalyst no-addition coke and CRI increased by 5–13 from 26.7 for the catalyst no-addition coke.

3.2.3. Initial Reaction Rate of the Catalyst-coated Cylindrical Coke

Figure 11 shows the weight loss of Fe-coated cylindrical
coke during the C–CO$_2$ reaction as a function of time. In
the initial stage of the reaction, the weight decreases in pro-
portion to time and the reaction rate is constant, however,
the reaction rate becomes slower as the weight loss in-
creases. Figure 12 also shows that during the C–CO$_2$ reac-
tion of the catalyst-coated nut coke, the weight decreases in
proportion to time and the reaction rate is constant until the
weight loss reaches 10%, however, the reaction rate be-
comes slower as the weight loss increases. Figure 13 shows
a comparison of the reaction rate of the catalyst no-addition
nut coke and the catalyst-coated nut coke at 0–5% weight
loss and 15–20% weight loss. Fe and Ca coated nut coke
show smaller reaction rate at 15–20% weight loss than at
0–5% weight loss, however, a still higher reaction rate than
the catalyst no-addition nut coke.

Figures 14(a) and 14(c) show the distribution of Fe and
Ca as determined using EPMA for the Fe- and Ca-coated
nut coke before reaction. It is clear that Fe and Ca is coated
only on the surface of the coke and the thickness of the
coating layer is approximately 0.05–0.2 mm. This implies
that in the case of the catalyst-coated coke, the reaction oc-
curs concentrated at the surface of the coke where the con-
centration of the catalyst is high and that the overall cat-
alytic activity decreases as the reaction site moves from the
surface to the inner core where the concentration of the cat-
alyst is low. On the other hand, as shown in Figs. 14(b) and
14(d), the catalyst (Fe and Ca) remains in the surface layer
of the coke after 20% weight loss, which suggests that the
reaction in the catalyst-coated surface layer is not com-
pleted at this stage. This assumption explains the fact that
at 15–20% weight loss Fe and Ca coated nut coke still show
a higher reaction rate than the catalyst no-addition nut coke.

Considering that the amount of solution loss reaction in
blast furnaces is at most 20%$^{2}$ and that an increase in the
initial reaction rate in the lower temperature range con-
tributes to decreasing the temperature of the thermal re-
serve zone, the catalyst-coated coke produced by the ‘post-
addition of catalyst to coke’ method has sufficient durabil-
ity of catalytic effects. The strength after the C–CO$_2$ reac-
tion for the catalyst-coated coke requires further study.
3.3. Evaluation of the Separation of the Catalyst Coated on Coke by Mechanical Impacts

Figure 15 shows the effect of drop impacts on the mass percentage of coke breeze evolution and the Fe content in the coke breeze. The amount of coke breeze increases with increasing the number of drop impacts, however, it levels off at approximately 1.6% after 3 to 4 drop impacts. On the other hand, the average Fe content in the coke breeze is approximately 11 mass%. Considering that the coke breeze is generated from the surface by abrasion, this shows that the concentration of Fe in the coke surface layer is 11 mass% on an average. The average content of Fe in the nut coke (20 mm in diameter) was 0.6 mass%. Assuming that (1) the Fe concentration in the coating layer on the coke surface is constant, 11 mass% and (2) the apparent density of coke is 1 g cm$^{-3}$, the calculated thickness of the Fe-coating layer is 0.185 mm, which corresponds well to the thickness measured by EPMA.

Figure 16 shows that the catalyst residual ratio (the ratio of the catalyst content in coke after mechanical impacts to that before impacts) is still as high as 70% after 10 times the drop impacts from 2 m height. There are many open pores and dents on the coke surface which the catalyst solution or slurry has easy access to and sticks to. Catalyst added in the form of solution or slurry is thought to penetrate into the open pores on the coke surface and the catalyst remains after the brittle coke surface is separated to generate coke breeze by drop impacts.

This suggests that the catalyst residual ratio might become smaller when the catalyst is coated on coke at the place where coke was less stabilized (e.g. the position closer to coke oven chambers in a commercial cokemaking plant) than in this study. On the other hand, the catalyst residual ratio might also become smaller when the catalyst is coated on coke with too much stabilization, since the surface of such coke becomes so smooth that there might be no dents on the coke surface to which the catalyst might stick. Therefore, we need to think carefully about the position where the catalyst is coated on coke in a commercial plant. According to the results of this study that the separation of the catalyst by mechanical impacts is suppressed when the catalyst is coated on the nut coke produced in a commercial plant, it seems preferable to add catalyst to coke between the coke cutter and the coke bin for a blast furnace.

There was a concern that the catalyst coated on the coke might be separated during the handling process of the coke (mechanical impacts through transportation and drops), however, this study reveals that the catalyst added as a form of solution or slurry penetrates into coke beyond the surface weak layer which can be easily separated as coke breeze by mechanical impacts and that 70% of the catalyst coated on the coke surface still remains after drop impacts. Moreover, as shown in Table 7, the reactivity (JIS R, J and CRI) of Fe-coated nut coke after drop impacts is a bit smaller than before drop impacts but still greater than before Fe-coating. This shows that the ‘post-addition of catalyst to coke method’ is effective as a way of increasing coke reactivity.

4. Conclusions

The characteristics of catalyst-coated highly reactive coke produced by the ‘post-addition of catalyst to coke’ method were investigated from the viewpoint of the reactivity, the durability of the catalytic effect and the separation of the catalyst coated on coke by mechanical impacts.

1. Fe and Ca coating on graphite, coke carbonized from deashed coal and blast furnace coke increased the reaction rate and decreased the reaction beginning temperature in an atmosphere closely resembling that in the thermal reserve zone in a blast furnace.

2. The reaction rate of Fe or Ca coated coke was kept high until the weight loss reached 10%, however, it becomes slower as the weight loss increases. On the other hand, the catalyst-coated coke shows a still higher reaction rate than the catalyst no-addition coke. This means that the catalytic effect is maintained high in the thermal reserve zone of the blast furnace.

3. After drop impacts, 70% of the catalyst coated on the coke surface still remains. The catalyst added in the form of solution or slurry penetrates into the open pores on the coke surface and the catalyst remains after the brittle coke surface is separated to generate coke breeze by drop impacts.

We will further study the post-reaction strength of the
catalyst-coated coke and also the effect of the catalyst-coated coke on the thermal reserve zone temperature with an adiabatic blast furnace simulator.

REFERENCES