Post-reaction Strength of Catalyst-added Highly Reactive Coke

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The development of production and utilization technology for highly reactive coke is significant in order to improve blast furnace reaction efficiency. In this report, the post-reaction strength of catalyst-added highly reactive coke was investigated. The reaction between coke and CO₂ was stopped at a weight loss of 20% and the reaction temperature was adjusted so that the reaction lasted for a constant period. In this experimental condition, the reaction temperature of highly reactive coke was lower than that of normal coke, which corresponds to the decrease in the thermal reserve zone temperature in a blast furnace. First, a decrease in reaction temperature made the reaction of the catalyst added coke more homogeneous, which increased the post-reaction strength of the highly reactive coke produced by the post-addition of catalyst to coke method; however, it decreased that of the highly reactive coke produced by the pre-addition of catalyst to coke method. Secondly, the post-reaction strength of catalyst-added highly reactive coke produced by the post-addition of catalyst to coke method became equal to or greater than that of normal coke. The types of catalysts and the catalyst adding method affect the porosity distribution in the coke after reaction and hence the post-reaction strength of coke to a great extent. Suitable selection of catalysts and its addition method to coke leads to highly reactive coke with post-reaction strength greater than that of normal coke. Catalyst-added highly reactive coke is a promising material to improve blast furnace reaction efficiency.

KEY WORDS: coke reactivity; catalyst; ironmaking; cokemaking; post-reaction strength; CSR; 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 required to produce 1000 kg of pig iron) as well as CO₂ 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 CO₂ (solution loss reaction C+CO₂=2CO). We have 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 are two basic methods of adding the catalyst to the coke: (1) the ‘post-addition of catalyst to coke’ method,³) where the catalyst and/or catalyst solution is coated onto the coke after the coke is pushed out of the coke oven chamber, and (2) the ‘pre-addition of catalyst to coke’ method,⁴,⁵) where the catalyst is mixed with coal before the mixture is carbonized in the coke oven chamber. As for the former method (1), we have reported⁶) that the reaction rate of Fe or Ca catalyst-coated highly reactive coke produced by the ‘post-addition of catalyst to coke’ method is kept high until the weight loss reaches 10% and that 70% of the catalyst coated on the coke surface still remains after the brittle coke surface is separated to generate coke breeze by drop impacts, since the catalyst penetrates into the open pores on the coke surface. As for the latter method (2), we have investigated the ‘pre-addition of Ca to coke’ method and reported⁷) that the use of the strong, highly reactive ‘lump’ Ca-rich coke produced by blending a Ca-rich coal in Muroran No. 2 Blast Furnace for a long period of time caused a decrease in the reducing agent rate.

From the viewpoint of CSR,⁶,⁷) a well-known index to evaluate the post-reaction strength of coke, CSR of highly reactive coke is generally low. CSR is the strength index after a constant period (2 h) of reaction and a highly reactive coke with higher CRI inevitably shows lower CSR. Due to its low CSR, there is a concern that the usage of highly reactive coke may promote the generation of coke breeze in a blast furnace and this is one of the barriers to the promotion of the usage of highly reactive coke in an actual blast furnace. In a sense, highly reactive coke could be underestimated.

On the other hand, it has been pointed out that the post-reaction strength of coke should be evaluated after a constant weight loss percentage since the amount of C consumed by the solution loss reaction in a blast furnace is almost constant.⁸–¹⁰) Nishi et al.¹¹,¹²) proposed a coke structure that is resistant to breakage after reaction: the coke of which the reaction follows the unreacted-core reaction
model (the coke with highly reactive carbon structure and low porosity, e.g. formed coke) and the homogeneous reaction model (the coke with less reactive carbon structure, high porosity and thick coke structure wall). Watakabe et al.\(^ {10} \) showed that the coke reaction occurred preferentially on the coke surface in the case of highly reactive coke. They also showed that the reaction degree gradient inside the coke lump was steeper in the case of highly reactive coke and that a highly reactive coke is more resistant to breakage after reaction. Yamaguchi et al.\(^ {13} \) reported that the coke reaction occurred preferentially on the surface of the coke and that of high CRI coke to the assumption that CO\(_2\) enters the inner part of the coke, which disperses the reaction through the entire particle. This comment is different from the view by Nishi et al.\(^ {11,12}\) and Yamaguchi et al.\(^ {13} \) attributed this difference to a difference in the reaction condition; in Yamaguchi’s study the reaction was conducted at an increasing temperature and in Nishi’s study the reaction was conducted at a constant temperature.

There are several opinions on the reaction degree gradient in a highly reactive coke after the reaction. It is suggested that the post-reaction strength of a highly reactive coke is higher than that of a normal coke\(^ {8,9}\) when the reaction was stopped at a constant weight loss percentage. Watakabe et al.\(^ {13} \) reported that an increase in the coke CRI decreased the ratio of the coke breeze in the coke sample taken out of the dead-man in an actual blast furnace. This suggests that it would be better to evaluate the post-reaction strength of the coke with a constant weight loss percentage in order to simulate an actual blast furnace.

However, there have been no systematic studies on the strength of the catalyst-added coke after the reaction with a constant weight loss percentage. Moreover, considering that a highly reactive coke would decrease the thermal reserve zone temperature in an actual blast furnace, it is necessary to study the effect of the reaction temperature on the post-reaction strength of the catalyst added coke; however, this is unclear. It is reported\(^ {8,11,14-16}\) that there is a reaction degree gradient (porosity gradient) inside the coke lump. It is also reported that at a higher reaction temperature the coke reaction occurs preferentially on the surface of the coke with the inner part of the coke lump being kept nearly unreacted\(^ {16,12}\). Furthermore, it is reported that at a lower reaction temperature the reaction gas diffuses into the coke inside\(^ {17}\), which makes the coke reaction mode more homogeneous\(^ {18}\). Since the reaction temperature has a great effect on the reaction degree gradient inside the coke lump, it is important to study the effect of the reaction temperature on the post-reaction strength of the catalyst added coke.

Therefore, in this report, we investigated the strength of the catalyst-added coke after the reaction test in which two of the three parameters (the weight loss percentage, the reaction time and the reaction temperature) were fixed.

### 2. Experimental

#### 2.1. Catalyst Addition to Coke

First, catalyst-added highly reactive coke was prepared by the ‘pre-addition of catalyst to coke’ method and the ‘post-addition of catalyst to coke’ method.

##### 2.1.1. ‘Pre-addition of Catalyst to Coke’ Method

The mixtures of coal and catalyst compounds were carbonized in the electrically heated test coke oven\(^ {19,20}\) to obtain highly reactive coke. The mixtures were prepared by adding catalyst compounds (Na\(_2\)CO\(_3\), Fe\(_3\)O\(_4\), and fine CaO powder\(^ {3}\)) to a blended coal (consisting of coals A 10%, B 10%, C 10%, D 20% and E 50% (Table 1), 85% <3 mm, moisture 4%) at an addition ratio of 2.5 mass%. After carbonization in the electrically heated test coke oven\( \times 200\) to 700 mm), moisture 4% at an addition ratio of 2.5 mass%. The sample was charged in a steel box (420 mm wide, 600 mm long and 400 mm high) at a bulk density of 850 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 1 250°C in an actual coke oven.

##### 2.1.2. ‘Post-addition of Catalyst to Coke’ Method

Next, two types of catalyst added coke were prepared by the ‘post-addition of catalyst to coke’ method. One is coke with the catalyst coated only on its surface and the other is the coke with the catalyst homogeneously dispersed. A preliminary test showed that vacuum-impregnation of coke in catalyst solution was effective for dispersing the catalyst homogeneously in the coke particle. Then a vacuum-impregnation method was used in the main test. 20±1 mm samples were prepared from the coke produced in an actual commercial plant. They were dipped in a catalyst solution (1) in vacuum for 60 min (abbreviated as ‘dipped in vacuum’) or (2) in atmospheric pressure for 10 min (abbreviated as ‘dipped in atmospheric pressure’). Various catalysts (NaCl, Fe(NO\(_3\))\(_3\) and CaCl\(_2\) were used to prepare 1.0 Na-mol/L, 0.9 Fe-mol/L and 1.0 Ca-mol/L aqueous solution of catalysts.

#### 2.2. Coke Strength Measurement

Coke strength was evaluated by \(I_{1000}\) (percentage of coke mass retained on a sieve with 9.5 mm apertures to the mass of the original coke sample after 600 revolutions (20 rpm\(\times 30\) min) in the I-type drum tester (\(\phi 130\times L 700\) mm)).

<table>
<thead>
<tr>
<th>Coal</th>
<th>Proximate analysis (mass % db)</th>
<th>Total dilatation (vol.%)</th>
<th>Maximum fluidity (log MF/ddpm)</th>
<th>Mean reflectance (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>VM</td>
<td>Ash</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>A</td>
<td>18.0</td>
<td>9.7</td>
<td>44</td>
<td>1.08</td>
</tr>
<tr>
<td>B</td>
<td>20.9</td>
<td>9.6</td>
<td>107</td>
<td>2.60</td>
</tr>
<tr>
<td>C</td>
<td>25.4</td>
<td>10.6</td>
<td>242</td>
<td>3.74</td>
</tr>
<tr>
<td>D</td>
<td>24.4</td>
<td>8.8</td>
<td>117</td>
<td>2.97</td>
</tr>
<tr>
<td>E</td>
<td>36.7</td>
<td>9.3</td>
<td>43</td>
<td>2.23</td>
</tr>
</tbody>
</table>

Table 1. Characterization of the coals used.
Table 2. The comparison of the CSR test and the macro thermobalance test.

<table>
<thead>
<tr>
<th>Sample</th>
<th>CSR test</th>
<th>Macro thermobalance test</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reaction atmosphere</td>
<td>CO₂, 100%</td>
<td>any CO₂/CO ratio (CO₂/CO=50/50 in this paper)</td>
</tr>
<tr>
<td>Reaction temperature</td>
<td>1100°C</td>
<td>any temperature</td>
</tr>
<tr>
<td>Reaction time</td>
<td>2h</td>
<td>(or any reaction time in this paper)</td>
</tr>
<tr>
<td>Weight loss</td>
<td>The weight is measured after the reaction. (Weight loss (%) = CRI)</td>
<td>The weight loss is recorded during the reaction. (The reaction was stopped at the weight loss of 20% in this paper)</td>
</tr>
<tr>
<td>Strength after reaction</td>
<td>+9.5mm after 600 revolutions in the I-type tester</td>
<td></td>
</tr>
</tbody>
</table>

2.3. Post-reaction Strength of Coke

2.3.1. Coke Strength after Reaction at a Constant Temperature for a Constant Period

The conventional CSR test\(^6,7\) corresponds to the evaluation of coke strength after reaction at a constant temperature for a constant period. In this test, 200 g of 20±1 mm coke was reacted with CO₂ at 1 100°C for 2 h and CRI (Coke Reactivity Index: the percentage of weight loss to the original coke mass after reaction) and CSR (Coke Strength after Reaction: \(I^C_{10}^{9.5}\); percentage of coke mass retained on a sieve with 9.5 mm apertures to the mass of the reacted coke sample after 600 revolutions in the I-type drum tester) were obtained.

2.3.2. Coke Strength after Reaction with a Constant Weight Loss at a Constant Temperature

Coke samples were reacted with CO₂ at 1 100°C until the weight loss reached 20% in the CSR test retort and post-reaction strength was measured. The reaction period necessary for obtaining 20% weight loss was determined based on CRI (the percentage of weight loss after 2 h of reaction) by assuming that the weight loss is proportional to the reaction period (i.e. the reaction rate is constant).

Furthermore, the reaction test was conducted with a macro thermobalance coke reaction simulator\(^21\) in order to evaluate the post-reaction strength of coke after reaction with a constant weight loss (20%) at a constant temperature under the reaction gas composition (CO₂/CO=50/50) closely resembling that in the thermal reserve zone in an actual blast furnace. A comparison of the conventional CSR test and the macro thermobalance test is shown in Table 2. The reaction gas is introduced into the reactor of the macro thermobalance coke reaction simulator from its bottom and the changes in weight with time can be recorded continuously by measuring the total weight of the sample and the reactor with the balance. In this test, 200 g of 20±1 mm coke was placed in the retort and heated up to the desired temperature in a N₂ atmosphere. Then the gas was changed to the reaction gas (CO₂/CO=50/50) and the changes in weight with time were monitored. When the weight loss reached 20%, the reaction was stopped by changing the reaction gas to N₂ and quenching the reactor. A reaction temperature between 1 000°C and 1 200°C was selected. Post-reaction strength was evaluated by \(I^C_{10}^{9.5}\), which is described as CSR(WL 20%, CO₂/CO=100/0) or CSR(WL 20%, CO₂/CO=50/50) depending on the composition of the reaction gas.

2.3.3. Coke Strength after Reaction with a Constant Weight Loss for a Constant Period

Furthermore, evaluated was the post-reaction strength of coke after reaction with a constant weight loss (20%) for a constant period under the reaction gas composition (CO₂/CO=50/50) closely resembling that in the thermal reserve zone in an actual blast furnace. In order to determine the reaction temperature where the weight loss reaches 20% after a certain period, first the coke with no catalyst addition was reacted at 1 100°C until the weight loss reached 20%. The reaction period was 131 min. Then the reaction temperature where the weight loss reaches 20% after 131 min was determined by assuming that the dependence of the reaction rate on temperature follows the Arrhenius’ equation. The coke sample was reacted at the temperature until the weight loss reached 20%. Post-reaction strength was evaluated by \(I^C_{10}^{9.5}\), which is described as CSR(WL 20%, Time=const. CO₂/CO=50/50).

2.4. Evaluation of Porosity Distribution in Coke

Porosity distribution in coke was analyzed by an image analysis in order to investigate the distribution of reaction degree in coke. First, 20 mm nut coke samples (both before and after reaction) were mounted in resin and their surface was polished. Then digital images of 16 consecutive fields (4 fields in a rank ×4 fields in a column) were taken with an optical microscope (objective lens ×2.5, eyepiece ×10) and 16 images were synthesized into a large photomicrograph as shown in Fig. 1(a). This image data was separated into 8 layers from the surface to the inside by a certain distance (0.25, 0.25, 0.5, 1, 2, 2 and 2 mm, in order from the surface) as shown in Fig. 1(b) and after binary image processing (Fig. 1(c)), the porosity of each layer was obtained. The porosity obtained by the image analysis technique depends on the condition of the binary image processing. Then the ratio of the porosity measured by the JIS method to the average of each layer’s porosity obtained by the image analysis was defined as a correction coefficient and the image analysis porosity data was corrected by multiplying the correction coefficient. The image analysis was conducted for two particles and the average value was obtained. It is reported that some of the coke surface disappears as a result of the reaction and that the thickness of the disappeared part decreases with decreasing the weight loss percentage.\(^11\) In this study, since the weight loss percentage is as low as 20% and constant, the analysis was conducted assuming that the coke surface does not disappear as a result of the reaction.
3. Results and Discussion

3.1. Coke Strength after Reaction at a Constant Temperature for a Constant Period

The concentration of Na, Fe and Ca in coke is shown in Table 3. The catalyst concentration in coke dipped in catalyst solution in vacuum was higher than that in coke dipped in atmospheric pressure as expected. CRI and CSR are shown in Table 3 and the relationship between CRI and CSR is shown in Fig. 2. The line in the figure is the approximation line calculated by the method of least squares. It is clear that CSR decreases with increasing CRI and that the coke produced by the pre-addition of catalyst to the coke method shows high CRI and extremely low CSR. Since the reaction period is constant in the CSR test, CSR of highly reactive coke is inevitably low.

3.2. Coke Strength after Reaction with a Constant Weight Loss at a Constant Temperature

Figure 3 shows the relationship between CSR and CSR(WL 20%, 1100°C, CO_2/CO/H_2 = 50/50) (the strength after the reaction (1100°C, CO_2/CO/H_2 = 50/50) stopped at a weight loss of 20%). CSR(WL 20%, 1100°C, CO_2/CO/H_2 = 100/0) of catalyst pre-addition coke is lower than that of no-catalyst addition coke; however, the difference in CSR(WL 20%, 1100°C, CO_2/CO/H_2 = 100/0) is 20 to 25, which is smaller than the difference in CSR, 40 to 60. CSR(WL 20%, 1100°C, CO_2/CO/H_2 = 100/0) of catalyst post-addition coke is close to that of no-catalyst addition coke. As shown in Fig. 4, the coke strength after the reaction (1100°C, CO_2/CO=50/50) stopped at a weight loss of 20% is nearly equal to the coke strength after the reaction (1100°C, CO_2/CO=100/0) stopped at a weight loss of 20%.

Figures 5, 6, 7 and 8 show the relationship between the reaction temperature and the strength after reaction (CO_2/CO=50/50) stopped at a weight loss of 20% for catalyst no-addition coke, catalyst pre-addition coke, catalyst post-addition coke, and catalyst pre-addition coke, respectively.

Table 3. The concentration of Na, Fe and Ca in coke, CRI and CSR.

<table>
<thead>
<tr>
<th>Substance</th>
<th>Addition method</th>
<th>key</th>
<th>Catalyst concentration in coke (mass%)</th>
<th>CRI (°)</th>
<th>CSR (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na</td>
<td>Pre-addition</td>
<td></td>
<td>0.03 0.38 0.13</td>
<td>27.4</td>
<td>61.4</td>
</tr>
<tr>
<td></td>
<td>dipped in vacuum</td>
<td>▲</td>
<td>1.11 - -</td>
<td>55.0</td>
<td>19.4</td>
</tr>
<tr>
<td></td>
<td>dipped in atmospheric pressure</td>
<td></td>
<td>0.27 - -</td>
<td>30.8</td>
<td>58.7</td>
</tr>
<tr>
<td>Fe</td>
<td>Pre-addition</td>
<td></td>
<td>- 2.41 -</td>
<td>47.0</td>
<td>7.8</td>
</tr>
<tr>
<td></td>
<td>dipped in vacuum</td>
<td>▲</td>
<td>- 2.44 -</td>
<td>49.4</td>
<td>33.0</td>
</tr>
<tr>
<td></td>
<td>dipped in atmospheric pressure</td>
<td></td>
<td>- 1.02 -</td>
<td>46.5</td>
<td>40.5</td>
</tr>
<tr>
<td>Ca</td>
<td>Pre-addition</td>
<td></td>
<td>- - 1.70</td>
<td>69.4</td>
<td>6.9</td>
</tr>
<tr>
<td></td>
<td>dipped in vacuum</td>
<td>▲</td>
<td>- - 1.22</td>
<td>35.4</td>
<td>58.5</td>
</tr>
<tr>
<td></td>
<td>dipped in atmospheric pressure</td>
<td></td>
<td>- - 0.49</td>
<td>39.2</td>
<td>49.1</td>
</tr>
</tbody>
</table>
post-addition (dipped in vacuum) coke and catalyst post-addition (dipped in atmospheric pressure) coke, respectively. As shown in Fig. 5, in the case of catalyst no-addition coke, CSR (WL 20%, CO₂/CO = 100/0) increases with decreasing temperature in the temperature range of 1000 and 1200°C. Nishi et al. [12] showed that the coke strength after reaction (CO₂/CO = 100/0) that stopped at a weight loss of 20% increased slightly with decreasing temperature in the same temperature range as in our study. Our study showed that a similar tendency was observed in the gas composition
closely resembling that in the thermal reserve zone in a blast furnace. In the case of Fe or Ca pre-addition coke, CSR(WL 20%, CO2/CO/H2 50/50) decreases with decreasing temperature (Fig. 6). On the other hand, in the case of catalyst post-addition coke, CSR(WL 20%, CO2/CO/H2 50/50) slightly increases with decreasing temperature (Figs. 7 and 8) regardless of the catalyst element. Figures 9 to 15 show the porosity distribution in coke after reaction. The slope of porosity distribution becomes gentle as the reaction temperature decreases. This suggests that as the reaction temperature decreases, CO2 enters the inner part of the coke more, which disperses the reaction through the entire particle and makes the reaction degree gradient gentler.

This implies that the reaction mode of the highly reactive coke produced by the post-addition of the catalyst to coke method becomes more homogeneous with decreasing the reaction temperature9,11,12,17,18) and that this change helps to enhance the post-reaction strength.

The strength (I 600) of the coke produced by the pre-addition of catalyst to coke method is lower than that of the catalyst no-addition coke as shown in Table 4. This is considered because an addition of catalysts that are non-fusible

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Fig. 9. The porosity distribution in coke after reaction (CO2/CO=50/50) stopped at the weight loss of 20% (catalyst no-addition coke samples).

Fig. 10. The porosity distribution in coke after reaction (CO2/CO=50/50) stopped at the weight loss of 20% (Na pre-addition coke samples).

Fig. 11. The porosity distribution in coke after reaction (CO2/CO=50/50) stopped at the weight loss of 20% (Na post-addition (dipped in atmospheric pressure) coke samples).

Fig. 12. The porosity distribution in coke after reaction (CO2/CO=50/50) stopped at the weight loss of 20% (Fe pre-addition coke samples).

Fig. 13. The porosity distribution in coke after reaction (CO2/CO=50/50) stopped at the weight loss of 20% (Fe post-addition (dipped in atmospheric pressure) coke samples).

Fig. 14. The porosity distribution in coke after reaction (CO2/CO=50/50) stopped at the weight loss of 20% (Ca pre-addition coke samples).

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inert substances inhibits the expansion and adhesion of coal particles. As the reaction gas diffuses into the inner part of coke at a low temperature range, the relatively weak structure of coke near the catalysts reacts selectively. This will increase the number of defects that could become the starting points of the coke breakage caused by impacts. In the case of the pre-addition of catalyst to coke method, a decrease in the reaction temperature might make the reaction mode more homogeneous and decrease the post-reaction strength of coke. In the case of Na pre-addition, a decrease in the reaction temperature did not decrease the post-reaction strength as shown in Fig. 6. CSR and CSR(WL 20%, 1100°C, CO2/CO/H2 50/50) of Na pre-added coke are higher than those of Fe and Ca pre-added coke (as shown in Fig. 3) although the strength (I1000) of Na pre-added coke is lower than that of Ca pre-added coke (as shown in Table 4). The reason for this is unclear and further study is required.

### Table 4. The characteristics of no-catalyst addition and catalyst pre-addition coke.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Catalyst addition method</th>
<th>Ash (mass%db)</th>
<th>I1000 (°)</th>
<th>Apparent density (g/cm³)</th>
<th>True density (g/cm³)</th>
<th>Porosity (%)</th>
<th>JIS coke reactivity index (-)</th>
</tr>
</thead>
<tbody>
<tr>
<td>No addition</td>
<td>No addition</td>
<td>11.61</td>
<td>87.6</td>
<td>1.08</td>
<td>1.89</td>
<td>42.6</td>
<td>22.6</td>
</tr>
<tr>
<td>Na2CO3</td>
<td>Pre-addition</td>
<td>13.79</td>
<td>82.9</td>
<td>1.01</td>
<td>1.87</td>
<td>46.1</td>
<td>50.8</td>
</tr>
<tr>
<td>FeO</td>
<td>Pre-addition</td>
<td>14.27</td>
<td>82.8</td>
<td>1.02</td>
<td>1.90</td>
<td>46.3</td>
<td>63.6</td>
</tr>
<tr>
<td>CaO</td>
<td>Pre-addition</td>
<td>14.60</td>
<td>85.8</td>
<td>1.03</td>
<td>1.92</td>
<td>46.2</td>
<td>65.7</td>
</tr>
</tbody>
</table>

### Table 5. Experimental condition and result in the post-reaction coke strength evaluation test after C–CO2 reaction (CO2/CO/H2 50/50) stopped at the weight loss of 20% under constant reaction time.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Target; weight loss 20%, reaction time 131 min</th>
</tr>
</thead>
<tbody>
<tr>
<td>Substance</td>
<td>Addition method</td>
</tr>
<tr>
<td>Na</td>
<td>Pre-addition</td>
</tr>
<tr>
<td></td>
<td>dipped in vacuum</td>
</tr>
<tr>
<td>Fe</td>
<td>Pre-addition</td>
</tr>
<tr>
<td></td>
<td>dipped in vacuum</td>
</tr>
<tr>
<td>Ca</td>
<td>Pre-addition</td>
</tr>
<tr>
<td></td>
<td>dipped in vacuum</td>
</tr>
</tbody>
</table>

### 3.3. Coke Strength after Reaction with a Constant Weight Loss for a Constant Period

Figure 16 shows an example of the relationship between the reaction temperature and the reaction rate. The relationship follows the Arrhenius’ equation. Based on this result, the reaction temperature at which the weight loss reaches 20% after a constant reaction period (131 min) was calculated and the reaction experiments were conducted near this temperature until the weight loss reached 20%. As shown in Table 5 the reaction periods of the experiment were close to the target reaction period, 131 min. Moreover, the reaction temperature for the catalyst-added cokes was lower than that for the catalyst no-addition coke, which corresponds to a decrease in the thermal reserve zone temperature in an actual blast furnace.

Figure 17 shows the relationship between CSR and CSRWL/20%, Time=const., CO2/CO/H2 50/50 (the strength after the reaction (CO2/CO=50/50) stopped at a weight loss of 20% after a constant reaction period). CSRWL/20%, Time=const., CO2/CO=50/50 for the catalyst pre-added coke is lower than that for the
catalyst no-addition coke; however, that for the catalyst post-added coke is close to or greater than that for the catalyst no-addition coke regardless of the dipping method (in vacuum or in atmospheric pressure).

Figures 18, 19 and 20 show examples of the porosity distribution in coke after the reaction stopped at a weight loss of 20% under constant reaction time. Regardless of the catalyst addition methods, the porosity distribution in coke after reaction for the catalyst added coke is gentler than that for the catalyst no-addition coke, which shows that the reaction mode becomes more homogeneous. The reaction mode of the catalyst post-addition (dipped in vacuum, Fig. 19) coke is the most homogeneous among these. The reason for this is considered as follows. In the case of the catalyst post-addition method dipped in vacuum, the inner part of the coke where the catalyst is fixed is connected to the outside of the coke through the channel pores. Therefore, even though the catalyst is fixed in the inner part of the coke through the vacuum-impregnation method, the reaction gas easily goes into the inner part of the coke where the catalyst is fixed. Then the reaction activated by the catalyst widens the channel pore, which further enhances the diffusion of the reaction gas into the inner part.

Furthermore, as shown in Fig. 19 in the case of Fe post-addition dipped in vacuum, the porosity distribution in the post-reaction coke is nearly uniform and the reaction mode for this coke is more homogeneous than that in the case of Na or Ca post-addition dipped in vacuum. One of the reasons is that the reaction temperature for the Fe added coke is much lower than that for the other cokes and another rea-
son is ascribed to the characteristics of Fe activity as a catalyst in the reaction atmosphere. The concentration of the reaction gas CO$_2$ in the coke decreases with increasing the distance from the coke surface due to the diffusion resistance and the CO$_2$ consumption by the reaction. In addition to this, in the C–CO$_2$ reaction, the product, CO, suppresses the reaction.$^{22}$ Therefore, it is considered that the reaction in the inner part of the coke is greatly suppressed due to the low concentration of CO, and the reaction suppressing effect by CO. On the other hand, Fe$^{3+}$ shows higher activity in the Coke–CO$_2$ reaction in the reaction gas containing more CO than in pure CO$_2$. Then the reaction in the inner part of the coke in the case of Fe post-addition dipped in vacuum could be promoted due to the co-existence of CO and Fe.

As shown in Fig. 17, CSR (WL 20%, Time=const., CO$_2$/CO=50/50) of the coke in the case of the catalyst post-addition dipped in vacuum is higher than that in the case of the catalyst post-addition dipped in atmospheric pressure. This implies that the selection of a suitable catalyst addition method could shift the reaction mode to a more homogeneous one at a lower reaction temperature, which leads to an increase in the post-reaction strength of coke.

As mentioned above, the strength after reaction with a constant weight loss for a constant period for the catalyst post-added coke could be close to or greater than that for the catalyst no-addition coke. It becomes clear that the adding methods and the types of catalyst have a great influence on the porosity distribution in the coke after the reaction and as a result on the post-reaction strength. When a catalyst added coke is used in an actual blast furnace, a detailed study on the coke from the viewpoint of the effect of the adding methods and the types of the catalyst on the post-reaction strength is necessary.

CSR is the strength index after reaction at 1100°C for a constant period (2 h) and is a useful and effective index for a blast furnace operation as long as the reactivity of the coke is normal. A highly reactive coke with higher CRI inevitably shows lower CSR. The reactivity of the catalyst-added highly reactive coke is too high to be evaluated by the conventional CSR test and should be evaluated with a different method such as the strength after reaction with a constant weight loss for a constant period investigated in this study.

4. Conclusions

We investigated the strength of the catalyst-added coke after the reaction test in which two of the three parameters (the weight loss percentage, the reaction time and the reaction temperature) were fixed.

(1) A decrease in the reaction temperature makes the reaction mode of the highly reactive coke more homogeneous and the slope of porosity distribution in the coke after reaction gentler. This change helps to increase the post-reaction strength of the catalyst post-added coke, however, decrease that of the catalyst pre-added coke. The selection of a suitable catalyst addition method could shift the reaction mode to a more homogeneous one at a lower reaction temperature, which leads to an increase in the post-reaction strength of coke.

(2) The strength of the catalyst post-added coke that was reacted under a condition similar to that in an actual blast furnace (until a constant weight loss percentage (20%) was reached at a constant temperature or for a constant period) could be close to or greater than that of the catalyst no-addition coke.

(3) The adding methods and the types of catalyst have a great influence on the porosity distribution in the coke after the reaction and as a result on the post-reaction strength.

This result infers that the selection of a suitable adding method and catalyst could increase the post-reaction strength of coke. We will further study the effect of the addition of the catalyst-added coke on the thermal reserve zone temperature with an adiabatic blast furnace simulator.

REFERENCES