Degradation Behavior of Coke at High-temperature Zone in Blast Furnace

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Synopsis
Coke properties at high temperature zones in a blast furnace play an important role for blast furnace operation. Therefore, with the advance of manufacturing technology on high strength of coke and its stability in the cold state, the interest for coke quality has been turned to that at high temperatures.

This report mainly describes the behavior of coke under high temperature conditions in a lower part of blast furnace.

In order to clarify the degradation behavior of coke in the blast furnace, a series of fundamental studies on the degradation of coke due to chemical, mechanical and thermal effects were carried out.

At Kashima No. 1 BF the sampling of coke has been done during the scheduled time of shutdown at three levels—lower shaft, bosh, and tuyere. The movement and accumulation of fine coke and the mutual relation between coke properties and the furnace performance were examined.

Based on the results of these studies and investigations, the mechanisms of degradation and disintegration of coke were discussed.

Key words: ironmaking; coke; blast furnace.

I. Introduction
Dissection examinations of blast furnaces clarified the changes of coke properties in the blast furnace. The coke particle size and strength begin to decrease in the lower part of the shaft level and extremely decrease near the tuyere level in a blast furnace. Concurrent with the dissection studies, extensive experiments on coke, such as operational trial of formed coke, comparison in an experimental blast furnace of low-grade coke and high-grade coke, combustion experiments by using an experimental blast furnace simulated to the lower part of actual blast furnace for a variety of coke and combustion tests in a small combustion furnace of several sorts of carbonaceous fuels were performed. Recently, examinations of properties of coke sampled at the tuyere and observation through a peep sight of tuyere by using high speed camera were performed. These experiments revealed that coke properties at high-temperature zones play an important role in a blast furnace operation.

Thus, the interest for coke quality was turned to that at high temperatures and the research on blast furnace operation was directed to methods of the evaluation of these properties of coke.

In order to clarify the degradation mechanism and the relation between the coke quality before charging and the furnace performance, fundamental investigations are required, such as experiments for reaction under simulated conditions of temperature, gas compositions and so on in the lower part of blast furnace.

From this point of view, through the investigation of coke samples taken out from the operating blast furnace, correlation between the coke behavior in a blast furnace and the blast furnace operation indices was examined. Next based on fundamental studies on the degradation of coke by gasification and thermal degradation, mechanism of degradation of coke in the lower part of the furnace was discussed.

II. Properties of Coke Sampled in Blast Furnace
At Kashima No. 1 BF the sampling of coke was performed during the scheduled time of shutdown at three levels (lower shaft, bosh and tuyere) to investigate the degradation of coke and the relation between blast conditions and degradation degree of coke.

1. Sampling Method of Coke from Blast Furnace
At the lower shaft level (S2) and the bosh level (B2) sampling was done at 8 points in the circumferential direction about 0.5~2 m from the wall and then total amount of 50 kg sample was used for analysis. Further total amount of 200 kg coke was sampled at the position of 6.5 m from the tuyere nose by a double-pipe type sampling probe which assured the sampling position from the tuyere nose.

The samples were divided into coke, metal, slag and coke with slag.

2. Change in Coke Properties
1. Change in Coke Strength and Particle Size
The longitudinal distributions of coke strength and mean size are shown in Fig. 1. Mean size was estimated from the weight fraction of coke over 5 mm considering the movement of coke fines. The fact that percentage of large particle size decreased and that of small particle size increased at S2 level after charging into furnace suggests that the coke degradation pattern is the surface abrasion type at this region.

On the other hand, the decrease in strength was remarkable at B2 level, while the change in mean size was little. The coke strength increased and the mean size decreased between B2 level and tuyere level. It is suggested that the weak part is exhausted and the coke strength apparently recovers. The generated coke fines are seemed to move upward accompanying gas.
2. Change in Coke Texture

After lump coke (+15 mm) was crushed under 200 mesh and packed with resin, coke texture was classified into the inert, isotropic and anisotropic with the microscope and point-counter. The longitudinal texture change is shown in Fig. 2. From stock level to B2 the ratio of isotropic texture decreases and that of anisotropic texture increases on the contrary. From B2 to tuyere level it was likely to increase in isotropic texture and decrease in anisotropic one. This recovery of texture to the original one before charging reveals that the surface layer of coke particle is reacted with CO2 gas and then it is exhausted in powder because of its weakness in the lower part of blast furnace.

III. Laboratory Investigation for High-temperature Properties of Coke

1. Experiment for Gasification of Coke at High Temperatures

In order to elucidate the coke behavior in the blast furnace it is very important to understand reaction behavior at high temperatures.

1. Experimental Procedure

Figure 3 shows the experimental apparatus used for the investigation. The coke of spherical shape (20 mmØ) suspended by platinum wire was charged into the reaction tube whose inner diameter was 70 mm. At first, sample was heated in an atmosphere of nitrogen (5 Nl/min) up to the predetermined temperature and was reacted by the reaction gas (15 Nl/min). The change in weight of coke was measured continuously by the use of a thermobalance for 2 h. The steam was generated by supplying refined water with a evaporation consist of the packed bed of alumina balls by the use of micro-quantitative pump.

Three kinds of coke having the characteristics shown in Table 1 were used as samples. Coke A has extremely low ash content and low reactivity. Coke B is commercial metallurgical coke. Coke C has low drum strength and high reactivity.

2. Experimental Results

In any case, the weight of coke was changed proportional to the time. The reaction rate was determined on the basis of this reaction curve. Figure 4 shows the relation between the weight loss of coke samples by gasification at 1100°C and the reaction rate of three kinds of coke with CO2, H2O, and O2 at 1 700°C.

When the reaction gas is H2O, the difference of reaction rate among three kinds of coke is considerably small. On the other hand, when the reaction gas is CO2 or O2, the difference among coke kinds is obvious. Therefore, CO2 reactivity test at 1100°C characterizes the coke behavior at high temperatures. When the coke shows higher rate of CO2 reaction, the rate of O2 reaction is also high. Although it
should be remembered that the reaction is dependent on the matrix carbon and the ash constituents, it is indicated that the reaction at high temperature zones, where the diffusion through the gas film is considered to be rate controlling step, is appreciably affected by the coke quality.

Figure 5 shows the deterioration of coke size by reaction. The solid line represents the relation when the reaction progresses at the surface. Although the relation of $O_2$ reaction is close to this line, the relations of $CO_2$ and $H_2O$ reaction are deviated upward.

When coke is reacted by $O_2$ there remains the unreacted zone within the particle. The reaction progresses near the surface and the intraparticle strength is maintained to be strong. On the other hand, when the reaction gas is either $CO_2$ or $H_2O$, it is presumed that the degradation of coke becomes significant.

2. Experiment for Rapid Heating of Coke

There are many factors that the coke is heated rapidly by the high temperature gas in the blast furnace. The degradation behavior of coke was investigated from the point of thermal degradation. The formation of crack on the remarkable intraparticle temperature gradient was examined by the fundamental experiment for rapid heating of coke and the results were discussed by the stress analysis within the coke particle.

1. Experimental Procedure

Figure 6 shows the experimental apparatus used for investigation. The intraparticle temperatures of coke of spherical shape during heating were measured by thermocouples ($3 \text{ mm}^2$) embedded into the center and the middle of the sample. The diameter of reaction tube was 100 mm.

The experiment was carried out by the following procedure. After the temperature in the reaction tube is held at the predetermined value for 30 min in an atmosphere of nitrogen, the coke embedded thermocouples described above is heated rapidly by being put into a reaction tube at a constant speed, and the changes in temperature at each point within coke particle are measured continuously.

When the temperature within coke particle is almost close to that of atmosphere, the experiment is stopped and the macrostructure of coke is observed after cooling to the room temperature.

The metallurgical coke having characteristics shown in Table 1 was used for the experiment. The formed coke carbonized at low temperature (named semi-formed coke) was used for a comparison and its characteristics is shown similarly in Table 1.

2. Experimental Results

Figures 7 and 8 show the typical measurements of change in intraparticle temperature for the metallurgical coke and the semi-formed coke, respectively. The heating speed of semi-formed coke is lower than that of metallurgical coke despite of similar experimental conditions. Nagasaka et al.\textsuperscript{12) reported that
the same results as shown in Fig. 8 were obtained when the coal briquette (fixed carbon 73.5%; volatile matter 19.0%; ash content 5.5%; moisture 2.0%) was heated rapidly. The reason why the semi-formed coke is heated slowly may be caused by the smaller heat conductivity due to the incomplete carbonization and the endothermic heat corresponding to the carbonization during heating.

Figure 9 shows the measurement of temperature at the center for various particle sizes. When the particle size is increased, the coke tends to be heated slowly and the time to close to the atmosphere temperature becomes long. Figure 10 shows the experimental measurements when the temperature in the reaction tube was changed. When the temperature in the reaction tube is increased, the coke tends to be heated rapidly at the beginning.

The crack was not formed on the experiments below 1300°C while the crack was observed beyond 1300°C.

Table 1. Main properties of sample cokes.

<table>
<thead>
<tr>
<th>Kind</th>
<th>Ash (%)</th>
<th>Apparent density (kg/m³)</th>
<th>Porosity (%)</th>
<th>Micro strength (+63 mesh%)</th>
<th>DI% (→)</th>
<th>CRI (%)</th>
<th>CSR (%)</th>
<th>Carbonization temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Metallurgical coke</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Coke A</td>
<td>0.7</td>
<td>1382</td>
<td>29.2</td>
<td>54.5</td>
<td>92.0</td>
<td>17.8</td>
<td>70.4</td>
<td>1100</td>
</tr>
<tr>
<td>Coke B</td>
<td>10.5</td>
<td>1081</td>
<td>41.0</td>
<td>53.8</td>
<td>93.5</td>
<td>32.4</td>
<td>57.1</td>
<td>1100</td>
</tr>
<tr>
<td>Coke C</td>
<td>10.8</td>
<td>1153</td>
<td>40.9</td>
<td>56.7</td>
<td>86.3</td>
<td>46.0</td>
<td>37.0</td>
<td>1100</td>
</tr>
<tr>
<td>Semi-formed coke</td>
<td>9.1</td>
<td>1121</td>
<td>37.5</td>
<td>38.7</td>
<td>91.6</td>
<td>48.1</td>
<td>35.6</td>
<td>560</td>
</tr>
</tbody>
</table>

IV. Discussion

1. Mechanism of Coke Deterioration at the High-temperature Zones of Blast Furnace

1. Degradation by Solution Loss Reaction

The influence of solution loss reaction on the strength of coke sampled in the blast furnace is shown in Fig. 11. The strength at B2 level decreases when the ratio of solution loss reaction increases. With respect to the changes in mean size and strength caused by the degradation of coke between B2 and tuyere level, the more the increase in strength was, the more coke was disintegrated. This phenomenon was caused by the severe chemical and physical conditions in the lower part of furnace and especially by the change in coke properties at the high temperature zones. It is presumed that the increase in porosity and the breakdown of the surface wall of coke pores due to the
solution loss reaction relate with the coke strength and cause the degradation of coke. It is indicated the carbon gasification has a great influence on the degradation of coke.

Figure 12 shows the difference of intraparticle distribution of fractional reaction and gas composition existing among two brands of coke calculated under the conditions of temperature and gas compositions measured by using vertical probe in the blast furnace. The calculation was carried out on the basis of following fundamental equations and boundary conditions.

Fundamental equations:
\[
\frac{d}{dr} \left( D_i \frac{dC_i}{dr} \right) + \frac{2}{r} D_i \frac{dC_i}{dr} - R_i = 0 \quad \text{(1)}
\]
\[
\frac{dC_i}{dt} = k_i (C_i - C_i^e) \quad \text{(2)}
\]
Boundary conditions:
\[
at r = r_s, \quad k_f (C_s - C_i) = D_i \frac{dC_i}{dr} \quad \text{(3)}
\]
\[
at r = 0, \quad D_i \frac{dC_i}{dr} = 0 \quad \text{(4)}
\]
where, 
- \( B \): bulk
- \( C_c \): concentration of carbon (mol/cm\(^3\))
- \( C_i \): concentration of gas \( i \) (mol/cm\(^3\))
- \( C_i^e \): equilibrium concentration of gas \( i \) (mol/cm\(^3\))
- \( D_i \): effective diffusion coefficient (cm\(^2\)/s)
- \( k \): reaction rate constant (cm/s)
- \( k_f \): mass transfer coefficient (cm/s)
- \( R \): reaction rate (mol/cm\(^3\)•s)
- \( r \): radius (cm)
- \( S \): particle surface.

When the temperature is 1000°C, the reaction proceeds uniformly within the particle. The higher the reactivity, the degree of overall reaction is the greater. On the contrary, when the temperature is 1400°C, the reaction zone is moved toward the particle surface. The difference of intraparticle of fractional reaction specifies the progress of deterioration in the high-temperature zones.

Through the above investigation for sampled coke in the blast furnace, coke is found to be degraded by the solution loss reaction at the following stages.

Carbon at the surface of coke is consumed due to the reaction between coke and CO\(_2\) and the coke size decreases. The intraparticle pore size is enlarged and the wall of coke becomes thinner. These phenomena cause the degradation of the macro strength and the formation of fine coke. In this manner, it is thought that the surface of coke is weakened and exfoliated, resulting in the degradation of coke size.

2. Degradation by Thermal Effect
If the coke is descended rapidly to the tuyere portion and is exposed to high temperature gas in the raceway, the thermal gradient within the particle becomes significant, to result in the increase of internal stress, and there exists a possibility that the crack is formed and the degradation is progressed.

Figures 7 to 10 show comparisons of temperature transition between the model predictions and the experimental measurements when the coke is heated rapidly.

The solid line is shown the transition of temperatures calculated by solving the rate equation of heat transfer (Eq. (5)) under boundary conditions expressed by Eqs. (6) and (7). The tendency of intraparticle temperature change with time is in good accordance with the experimental results. Particularly, thermal gradient near the surface is significant.

Fundamental equation:
\[
\rho C_p \frac{\partial T}{\partial t} = k \left( \frac{\partial^2 T}{\partial r^2} + \frac{1}{r} \frac{\partial T}{\partial r} \right) + 2 \rho_0 (T_b - T) + \sigma \varepsilon (T_b^4 - T^4) \quad \text{(5)}
\]
Boundary conditions:
\[
at r = 0, \quad \frac{\partial T}{\partial r} = 0 \quad \text{(6)}
\]
\[
at r = r_0, \quad k_c \frac{\partial T}{\partial r} = h_b (T_b - T) + \varepsilon \sigma (T_b^4 - T^4) \quad \text{(7)}
\]
where, 
- \( C_p \): specific heat (kcal/kg•K)
- \( \varepsilon \): blackness (-)
- \( h_b \): heat transfer coefficient (kcal/m\(^2\)•s•K)
- \( k_c \): effective thermal conductivity (kcal/m\(^2\)•s•K)
- \( r \): radial position (mm)
- \( t \): time (s)
- \( T, T_b, T_w \): temperature of coke, bulk gas, and reaction tube wall, respectively (K)
- \( \delta \): Stefan–Boltzmann constant (kcal/m\(^2\)•s•K\(^4\))
- \( \rho \): density (kg/m\(^3\)).
The above intraparticle temperatures are reflected to the theoretical stress analysis.

Figure 13 shows the changes in intraparticle temperature, tangential stress and radial stress when the cokes were heated rapidly at 1300°C, obtained by solving three simultaneous equations from Eqs. (8) to (10) under boundary conditions.

\[ \frac{da_r}{dr} + 2r \cdot (a_r - a_\theta) = 0 \] ...........................(8)

\[ \frac{du}{dr} = \frac{1}{E} \cdot (a_r - 2a_\theta) + \int_{t_0}^{t} \alpha d\tau \] ...........................(9)

\[ \frac{r}{u} = \frac{1}{E} \cdot [(1 - 2\nu)a_r - \nu a_\theta] + \int_{t_0}^{t} \alpha d\tau \] ...........................(10)

where, \( \alpha \): linear expansion coefficient (1/K)

\( a_r \): radial stress (kg/mm²)

\( \sigma_\theta \): tangential stress (kg/mm²)

\( \nu \): Poisson’s ratio (-)

\( E \): Young’s modulus (kg/mm²)

\( u \): displacement (m).

As the specific heat of metallurgical coke, the data by Agroskin13 is used. It has been reported by many researchers13-15) that the behavior of specific heat during carbonization is very complex. Therefore the value of semi-formed coke is assumed to be equal to that of metallurgical coke because the semi-formed coke is heated up to 500°C.

The thermal conductivity of metallurgical coke is given by Tadokoro.14 Miura et al.15 measured the thermal conductivity of various brands of coal during carbonization. However for the materials after the heat treatment has not been done. Then for the semi-formed coke, the computation of temperature change at center is repeated by assuming the thermal conductivity and the value when the model prediction is in fair agreement with the experimental measurement is used.

Poisson’s ratio and Young’s modulus are used by 0.35 and 9600 for metallurgical coke and 0.17 and 1000 for semi-formed coke measured at room temperature, respectively.

The heating speed of metallurgical coke is higher and the difference in intraparticle temperature is smaller than those semi-formed coke. This is because of the difference in thermal conductivity. According to the tangential and radial stress distributions, the expansion proceeds up to 1100°C, and then the contraction occurs for the metallurgical coke. While change from the expansion to contraction rises at about 500°C in accord with carbonization temperature for the semi-formed coke similar behavior qualitatively to that of metallurgical coke.

In general, the expansion progresses up to the carbonization temperature, and then the contraction occurs when the coke is heated. The intraparticle stress distribution is controlled by these expansion and contraction. The tangential stress on the inside is tensile stress and that at the surface is compressive.

Fig. 13.
Changes in intraparticle temperature, tangential stress and radial stress of coke.

(a) Metallurgical coke
(b) Semi-formed coke
stress until the surface temperature reaches to the carbonization temperature. The radial stress is tensile stress. When the surface temperature exceeds the carbonization temperature and the contraction begins to occur at the surface, the tangential stress is changed to compressive stress.

It is presumed that the cracks are formed when the stress goes beyond the tensile strength of coke and there exists two kinds of crack in a blast furnace. One is such a breakage as the spherical thin layer is exfoliated and the other is such a breakage as the coke is split from surface to inside. The former is caused by the radial tensile stress when the coke is heated below the carbonization temperature and the latter is caused by the tangential tensile stress when the coke is heated over the carbonization temperature.

3. Degradation by the Impact of Blast

The coke size degrades as it becomes porous and brittle by solution loss reaction and is subjected to mechanical impact in the raceway. The relation between the blast conditions and coke size distribution in a raceway is unclear.

The effect of blast velocity on the degradation of coke at Kashima No. 1 BF shown in Fig. 14. It is noted that the degradation of coke caused by the collision becomes remarkable according to the increase in blast velocity and the fraction of fine coke increases in the dead man. As a result, the permeability of the dead man decreases and the gas–coke heat exchange become insufficient so that the temperature of dead man decreases as shown in Fig. 15. On the contrary, under the lower blast velocity region the weight fraction of fine coke is less and the permeability in the dead man is good. However the depth of raceway decreases because the horizontal vector of the blast velocity decreases and consequently the temperature of dead man decreases. Therefore, the most appropriate blast velocity exists from the view point of both the prevention of coke degradation and the active dead man. It seems to be around 240 m/s at Kashima No. 1 BF.

2. Movement of Fine Coke Particles

The difference of estimated temperature from lattice constant between fine coke (≈3 mm) and lump coke (≈15 mm) is shown in Fig. 16. At bosh level (B2) and lower shaft level (S2) the temperature of fine coke was higher than that of lump coke by 200–250°C, and the temperature of fine coke at B2 level was as same as that of tuyere level. By the two-dimensional mathematical model and the cold model experiment concerning the two phase flow of gas and solid in a packed bed, fine coke generated in the lower part of blast furnace is estimated to move upward and accumulate in the zone where the gas velocity decreases remarkably. According to these facts, it is estimated that the fine coke generated near the tuyere level moves upward and then accumulates near B2 level.

3. Behavior of Coke in the Blast Furnace Caused by the Decrease in High Temperature Properties of Coke

The behavior of coke and various phenomena in the blast furnace have been discussed above. In accordance with these informations, Fig. 17 shows the effect of coke properties at high temperatures on the blast furnace operation and coke behavior.

When the coke reactivity increases, the region of indirect reduction reaction becomes narrow due to the decrease in beginning temperature of solution loss reaction and the furnace heat level, that is, hot metal temperature is decreased due to the increase in amount of reaction. Because the heat action is required to recover the hot metal temperature, the fuel rate increases.
On the other hand, the coke is weakened by the gasification due to solution loss reaction in the shaft and the degradation of coke is progressed by the decrease in postreaction strength.

Furthermore, when the fragile coke descends to the tuyere region, the thermal degradation of this coke tends to become significant and it suffers the remarkable generation of coke fines. The generated coke fines are accumulated in the region where the velocity of gas flow is low.

V. Conclusion

In order to clarify the degradation of coke in the blast furnace, at Kashima No. 1 BF, during the scheduled shut-down periods the coke samples were taken out at three levels—lower shaft, bosh, and tuyere. The movement and accumulation of fine coke and mutual relation between coke properties and the furnace performance were examined. In addition, a series of laboratory tests on the degradation of coke due to chemical, mechanical and thermal effects were carried out.

Based on the results of these studies and investigations, the mechanisms of degradation and disintegration of coke were discussed.

The following results are obtained.

(1) The degradation of coke was remarkable at the lower part of blast furnace, and the ratio of fine coke and the recovery of coke strength were increased. The carbon gasification by the solution loss reaction has a great influence on the degradation of coke.

(2) The thermal stress is related closely to the expansion and contraction of coke. It is presumed that the cracks are formed when the stress goes beyond the tensile strength of coke.

(3) In the blast furnace, there exist two kinds of cracks. One is such a breakage as the spherical thin layer is exfoliated and the other is such a breakage as the coke is split from surface to inside.

(4) The tuyere blast velocity have a great influence on the degradation of coke. The most appropriate blast velocity exists to satisfy the prevention of the inactive deadman and the remarkable degradation of coke.

(5) The fine coke particle generated in the lower part of blast furnace is estimated to move to the deadman or upward and accumulate according to the longitudinal distribution of the coke strength and in addition to the comparison of estimated temperature between fine and lump coke.

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