Effect of Coke Reactivity on Sinter Softening-melting Property by Simultaneous Evaluation Method of Carbonaceous and Ferrous Burdens in Blast Furnace

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In future blast furnace operation which aims at low carbon consumption, it is indispensable to optimize the quality of carbonaceous and ferrous burdens, not evaluations of each individual but both sides of them considering interactions under the coexistence. Therefore, a simultaneous evaluation method of carbonaceous and ferrous burdens at cohesive zone of blast furnaces by softening-melting test which simulated the temperature profile in blast furnaces determined by reactivity of coke was developed. The effect of sinter ore reducibility and coke reactivity on sinter softening-melting property at cohesive zone of blast furnaces were evaluated. With increasing CRI, coke reactivity, gasification start temperature lowers as a result of increasing the reduction rate of sinter at 900–1,000°C and increasing softening shrinkage resistance at the initial stage of the shrinkage near 1,200°C.

KEY WORDS: blast furnace; coke; sinter; reactivity; softening-melting test; permeability; shrinkage.

1. Introduction

When the self-fluxing sinter began to be used at the blast furnace in the second half of the 1950s, as property of sinter which is necessary to keep good permeability in blast furnaces the high cold strength and the proper diameter and the restraint of reduction degradation have been emphasized. Moreover, after the existence of the cohesive zone was identified by investigation of dissection of blast furnaces since the 1970s, the ore quality evaluation such as a load softening shrinkage, high temperature reduction until dripping and permeability has been carried out by softening-melting test.

After that, as the measure for keeping permeability which accompanies increasing PCI in the raw material supply situation change such as limonite increase in the 1990s, low slag and low SiO₂ sinter has been promoted. In addition to the control by cold strength up to then, the high-temperature permeability (KS value) has been estimated again. The KS value of sinter undergoes the effect by reducibility and gangue. Sinter reducibility at 900°C (e.g. JIS-RI) is almost corresponds to reducing ability near gasification start temperature of coke which is a source of the reducing-gas in blast furnaces. Also, the high reactivity coke has effect of reduction degree improvement by the shift to the lower temperature side of the reduction equilibrium point in the blast furnace. On the high reactivity coke, it has partially argued like above mentioned, because after the blast furnace enlargement in 1960’s, the required coke property becomes a high-strength direction and in the steelworks side which emphasized the productivity, coke strength should have priority over other coke property.

However, in the blast furnace operation which faces the global environmental issue and the resource depletion issue in which the discussion becomes rapidly active for recent 10 years, for both ore and coke high reactivity are noticed again from the viewpoint which aims at the low carbon consumption and the efficient use of inferior quality raw materials with the change of raw material supply and demand in the future. For example, research on ferro coke and carbon composite iron ore by the blast furnace use test in a past becomes active again.

When the quality of carbonaceous and ferrous burdens is optimized, not individual evaluation each but evaluation from both sides considering their interactions are indispensable. From this point of view, there are several studies. The adiabatic BIS furnace which applied the principle of Boris furnace, the method for using the on-line mathematical simulator jointly, and ASAM methods which are considered reaction time and the temperature profile change. However, there are comparatively few cases which evaluated simultaneously under the coexistence of carbonaceous and ferrous material.

Therefore, in this paper, evaluation was made from the basic experiment about the effect which the sinter reduci-
bility and the coke reactivity exert on the high-temperature permeable resistance at the cohesive zone. The change of the temperature and the gas composition profile in the blast furnace must be changed according to the coke reactivity when evaluating the effect which the coke reactivity exerts on the high-temperature permeable resistance at the softening-melting test. First, the independent gasification reaction experiment of coke was performed beforehand and the relation among coke reactivity, temperature, and gas composition were obtained. Secondly using this result, the effect which coke and sinter property exert on ore reduction, solution-loss, the high-temperature permeable resistance (KS value) by giving a heat pattern according to the coke reactivity as the condition of the softening-melting dripping experiment was evaluated. It is necessary to consider the effect on the reaction behavior by contraction and layer structure change with the fusion process in the lower part of cohesive zone in blast furnaces.

Hence, in this paper the method for evaluating high temperature reactivity and softening-melting property was developed by raw material packed bed with sufficient height including not only ore but also coke was composed.

2. Experiment and Method

2.1. Procedure of Evaluation Method

Near 900–1000°C region in which the coke starts the gasification in blast furnace, a reduction rate is comparatively small, because the CO, CO₂ composition is in the vicinity of reduction equilibrium, and it is changed by sinter ore composition such as calcium ferrite. Therefore, it is necessary to investigate the reaction of the reduction equilibrium Fe–FeO vicinity in detail. The procedure of simultaneous evaluation method for carbonaceous and ferrous burden property in the cohesive zone is following.

First of all, by gasification experiments on using coke with different reactivity, the effect which the reactivity exerts on the gasification starting temperature by the reaction rate analysis is obtained (Experiment 1). Next, when a coke gasification starting temperature is changed, in order to confirm the effect to exert on the temperature of thermal reserve zone in the blast furnace, the experiment of coupling reaction of the coke gasification and the ore reduction on the gas composition CO–CO₂ in the reducing reaction equilibrium Fe–FeO vicinity was carried out (Experiment 2). Using the temperature and gas composition pattern by each coke reactivity obtained at experiment 1, 2, the softening-melting experiment was carried out (Experiment 3). So the effect which the coke and the sinter property exert on the high-temperature permeable resistance is evaluated. Figure 1 shows the experimental apparatus and the conditions of Experiments 2 and 3 are shown in Fig. 2.

2.2. Specimen for Tests

2.2.1. Coke

A list of property of coke used in this study is shown in Table 1. On the basis of an actual blast furnace use blended coal, the reactivity was changed in a cold strength IS1600+9.5 to be 85±3%. It was described in the table sequentially from the left by a low reactivity CRI, and on the right side from C01 column in the table, there are high reactivity coke, CRI>40. C01, C02, C03, C08 and C11 were produced by an
actual coke oven and others were manufactured by a small electric furnace. DI³₁₀ is (>50 mm, 10 kg) before particle size adjustment immediately after product, and CRI and CSR are the analytical values of (20 mm, 200 g) after particle size adjustment for the experiment. The industrial analysis was by JIS M 8812, the ash content chemical analysis was by JIS M 8815, apparent density and the real density are the measurement values by JIS K 2151. Also, the pore-size analysis was by JIS M 8812, the ash content chemical analysis was by JIS M 8815, apparent density and the real density are the measurement values by JIS K 2151.

2.2.2. Sinter

It was described in the table sequentially from the left by C01, C02, C03, C04, C05, C06, C07, C08, C09, C10, C11, and C12. The list of the sinter property is shown in Table 2.

The list of the sinter property is shown in Table 2. It was described in the table sequentially from the left by C01, C02, C03, C04, C05, C06, C07, C08, C09, C10, C11, and C12. The list of the sinter property is shown in Table 2.

### Table 1. Chemical compositions and physical properties of coke used in the experiment.

<table>
<thead>
<tr>
<th>Coke</th>
<th>C01</th>
<th>C02</th>
<th>C03</th>
<th>C04</th>
<th>C05</th>
<th>C06</th>
<th>C07</th>
<th>C08</th>
<th>C09</th>
<th>C10</th>
<th>C11</th>
<th>C12</th>
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<tr>
<td>CRI  (%)</td>
<td>25.9</td>
<td>28.6</td>
<td>29.5</td>
<td>32.9</td>
<td>33.2</td>
<td>38.5</td>
<td>38.6</td>
<td>40.1</td>
<td>42.2</td>
<td>43.4</td>
<td>44.4</td>
<td>45.1</td>
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<tr>
<td>CSR  (%)</td>
<td>67.1</td>
<td>60.5</td>
<td>60.1</td>
<td>49.8</td>
<td>50.7</td>
<td>42.7</td>
<td>40.7</td>
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<td>42.3</td>
<td>41.4</td>
<td>34.4</td>
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<td>DT³₀⁻₁₀ (%)</td>
<td>84.8</td>
<td>75.0</td>
<td>85.0</td>
<td>82.5</td>
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<td>82.2</td>
<td>81.2</td>
<td>80.2</td>
<td>83.6</td>
<td>83.9</td>
<td>80.9</td>
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<tr>
<td>F₀⁻₀.₀₅ (%)</td>
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<td>85.4</td>
<td>87.1</td>
<td>82.2</td>
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<td>84.6</td>
<td>84.7</td>
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<td>87.0</td>
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<td>VM (%)</td>
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<td>0.50</td>
<td>1.08</td>
<td>0.50</td>
<td>0.42</td>
<td>0.60</td>
<td>0.50</td>
<td>0.59</td>
<td>0.40</td>
<td>0.77</td>
<td>0.60</td>
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<td>FC (%)</td>
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<td>87.8</td>
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<td>88.6</td>
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<td>Ash (%)</td>
<td>10.6</td>
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<td>11.8</td>
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<td>11.1</td>
<td>12.8</td>
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<td>SiO₂ (%)</td>
<td>56.5</td>
<td>55.0</td>
<td>58.0</td>
<td>56.5</td>
<td>56.7</td>
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<td>50.4</td>
<td>57.3</td>
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<td>AI₂O₃ (%)</td>
<td>31.1</td>
<td>29.6</td>
<td>26.0</td>
<td>28.7</td>
<td>31.6</td>
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<td>2.90</td>
<td>2.10</td>
<td>2.90</td>
<td>2.53</td>
<td>3.71</td>
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<td>4.53</td>
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<td>MgO (%)</td>
<td>0.88</td>
<td>0.98</td>
<td>1.10</td>
<td>0.85</td>
<td>1.43</td>
<td>0.83</td>
<td>0.89</td>
<td>1.70</td>
<td>1.98</td>
<td>0.67</td>
<td>1.43</td>
<td>1.39</td>
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<td>TFe (%)</td>
<td>3.58</td>
<td>3.22</td>
<td>4.50</td>
<td>3.81</td>
<td>3.63</td>
<td>3.39</td>
<td>3.84</td>
<td>5.09</td>
<td>4.46</td>
<td>3.31</td>
<td>3.63</td>
<td>11.8</td>
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<td>Apparent density*1 (g/cm³)</td>
<td>1.15</td>
<td>1.00</td>
<td>1.00</td>
<td>1.04</td>
<td>1.02</td>
<td>1.04</td>
<td>0.99</td>
<td>0.99</td>
<td>0.93</td>
<td>1.01</td>
<td>1.01</td>
<td>0.98</td>
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<tr>
<td>True density (g/cm³)</td>
<td>1.87</td>
<td>1.95</td>
<td>1.80</td>
<td>1.95</td>
<td>1.94</td>
<td>1.95</td>
<td>1.95</td>
<td>1.96</td>
<td>1.98</td>
<td>1.96</td>
<td>1.95</td>
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<tr>
<td>Total porosity*3 (%)</td>
<td>38.5</td>
<td>48.8</td>
<td>44.4</td>
<td>46.7</td>
<td>47.4</td>
<td>42.2</td>
<td>49.5</td>
<td>46.8</td>
<td>53.0</td>
<td>43.6</td>
<td>48.2</td>
<td>49.7</td>
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<tr>
<td>Large porosity (=150 μm)*2 (%)</td>
<td>1.20</td>
<td>13.5</td>
<td>8.80</td>
<td>11.9</td>
<td>11.4</td>
<td>5.10</td>
<td>10.5</td>
<td>10.1</td>
<td>14.2</td>
<td>9.70</td>
<td>19.1</td>
<td>11.7</td>
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<td>Middle porosity (10–150 μm)*2 (%)</td>
<td>24.6</td>
<td>22.0</td>
<td>23.9</td>
<td>23.1</td>
<td>29.3</td>
<td>25.3</td>
<td>30.3</td>
<td>19.8</td>
<td>28.7</td>
<td>23.4</td>
<td>18.1</td>
<td>27.9</td>
</tr>
<tr>
<td>Micro porosity (&lt;10 μm)*2 (%)</td>
<td>12.7</td>
<td>13.3</td>
<td>11.7</td>
<td>11.7</td>
<td>6.70</td>
<td>11.9</td>
<td>8.70</td>
<td>17.0</td>
<td>10.1</td>
<td>12.4</td>
<td>1.0</td>
<td>10.1</td>
</tr>
</tbody>
</table>

shown in Fig. 1(a). A coke sample is formed to globular shape (20±1 mm\(\phi\) and 17.5±1 mm\(\phi\)) by a grinder processing, and one particle was placed in the basket which is made from the platinum and protected with alumina. The basket was hang on the load-cell by platinum wire. A reaction rate was calculated by continuously measuring weight variation. Reaction gases were CO\(_2\)–N\(_2\)(20/80) system and CO–CO\(_2\)–N\(_2\)(20/20/60) system. All gas flow volume were 20 Nl/min, the experiment temperature was measured with the thermocouple placed immediately below the sample, and was changed from about 800°C to 1 200°C. In the experiment, the inside of the furnace was maintained at the constant pre-arranged temperature in the N\(_2\). After reaction starts, if the reaction rate reaches 25% in a carbon weight decrement rate or the reaction time pasts 4 hours, the experiment is terminated and cooling is started by changing the reaction gas to N\(_2\). The gasification reaction rate was calculated from the weight loss rate by the reaction. The sphere coke after the reaction was sliced in the radial direction after fixing it with the methyl metha acrylate resin of the super fast-dry, having kept penetration in the pore at the minimum, and the mapping by EPMA as shown in Fig. 3. The reaction seems to have mainly been generated from the peripheral part of the particle. Thus the linear analysis of carbon composition of the section was performed. Carbon distribution in radial direction in particle was measured and reaction rate distribution in particle was calculated from the relative value of count per sec (CPS).

2.3.2. Experiment 2: Coupling Reaction at Near Reduction Equilibrium Vicinity

Effect of coke reactivity on reducing reaction at the gas composition CO–CO\(_2\) system which is near reduction equilibrium Fe/FeO in the vicinity of thermal reserve zone was evaluated by the experimental apparatus shown in Fig. 1(b). In the stainless crucible with an inner diameter of 70 mm\(\phi\) with the ventilation holes which were in the crucible bottom, coke bed was placed in the bottom and sinter bed is laid with in the upper part, each thickness was 75 mm and diameter of both burdens are 15–20 mm. Coke used as an experiment 2 were C02 (CRI=28.6) and C08 (CRI=42.2) and sinter used with them is S04 (RI=65.3). The temperature is increased in the N\(_2\) until the pre-arranged temperature, 950°C, 1 050°C, and 1 150°C reaches. The reaction gas (25 Nl/min) was supplied Fe/FeO equilibrium gas composition in CO–CO\(_2\) system according to each temperature.

2.3.3. Experiment 3: Softening-melting Property

As shown in Fig. 1(b), the equipment independently controllable upper and lower graphite heating elements, and the soaking band length was secured about 400 mm (±20°C). A crucible and a guide pipe were made from graphite (diameter of 70 mm) with the sample filling layer height of 300 mm. The sample of sinter and coke with diameter of 15–20 mm comprises 4-layer structure and the height of each layer is 75 mm as shown in figure. Also, dissolved loss of upper rosutoru which is made from graphite was restrained by arranging about 15 mm thickness (one particle unit size) coke layer at the top and causing FeO(l)–C(s) reduction by the blowing up of the slag by coke. A thermocouple for the temperature measurement is installed in the sample bed top and a load is controlled with the graphite punch bar through graphite rosutoru. The temperature increase and the change of the gas composition are given as a typical pattern up to 1 650°C for about 6 hours as shown in Fig. 2. The temperature is increased in the N\(_2\) atmosphere until it reaches 200°C and N\(_2\) was switched to reaction gas. When the sample temperature reaches 800°C, the load become to 98 kPa. When the coke reactivity CRI increases, considering the reaction start temperature decrease, the temperature and the gas composition profile pattern was changed to the low temperature side based on Fig. 8, later described in chapter 3.1.

Dripping status on the turn table in the lower part is visually observed and a dripping temperature is recorded. During experiments, sample temperature, gas composition, gas volume rate, pressure-drop and displacement of the bed are continuously measured and KS is calculated from Eq. (1).
Here, as for $\Delta L$ was defined by the whole filling layer which includes a sinter layer and a coke layer, not only a sinter layer described in chapter 2.2. $T_c$ is not fix 1600°C but a shrinkage completion temperature measured every each case.

After the experiment, the droplets, residues, and dusts are separated to slag, metal, and carbon materials. And the weight loss of all graphite materials exposed reactant gas was measured.

In this experiment, the graphite material quality (ash <50 ppm) was chosen so that carbon of graphite material loss may become 30% or less of all carbon material in the above standard condition and sufficient airtightness. When reduction and gasification rate are calculated from exhaust gas composition and integration flow rate, inlet flow rate is corrected within about ±1 Nl/min, from the material balance based on coke, graphite material, carburation in dripped metal and dust in off gas stuck around the crucible.

3. Results and Discussion

3.1. Effect of Coke Reactivity on Reaction Start Temperature (Experiment 1)

3.1.1. Evaluation Method

It assumes that coke particle is a sphere shape and the solution loss reaction $\text{C} + \text{CO}_2 \rightarrow 2\text{CO}$ considering a gas diffusion in particle and a porosity change is described as follows.31) The mixed gas flux $J_i$, which is accompanied by the diffusion inside coke particle is the mole concentration gradient of species $j \Delta X_j$ where the constant of which is coefficient of $i$th and $j$th gas diffusion $D_{ijh}$ in particle, and it is expressed in the multicomponent system expanded Fick’s law as shown in Eq. (3)

$$J_i = \rho \frac{w_i}{w} \sum_{j=1}^{m} w_j D_{ij} \nabla X_j$$ ........................ (3)

where $w_i$ is the molecular weight of species $i$, $\text{wt}$ is the mean molecular weight of the mixture and $\rho$ is the gas mixture density. And, it is established by the reaction generation term $R_{i,m}$ for the gas flux change, it becomes

$$\frac{\partial}{\partial t} + \nabla J_i = R_{i,m}$$ ........................ (4)

when supposing the pseudo-stationary of the system here, omitting first term, so substituting Eq. (3), then Eq. (4) is expressed as simple Poisson type. Then, it is possible to solve under polar coordinates by giving a boundary condition in the central part: no concentration gradient ($dX/dr=0$) and in a boundary film: mass transfer which multiplied bulk and particle surface concentration gradient by $k_m$ which is expressed as Nelson’s equation.32) Effective coefficient of diffusion $D_{ijh}$ in Eq. (3) is expressed like Eq. (5), by valid porosity for diffusion which excluded closed pore $\epsilon_c$ from the coefficient of molecular diffusion $D_m$ and porosity $\epsilon$, and it considers increase of the coefficient of diffusion by the reaction. Also, $R_{i,m}$ is defined by Eq. (6) which contains the reaction promotion term $k_1$ by $\text{CO}_2$, and restraint term $k_2$ by $\text{CO}$.

$$D_{ijh} = D_m (\epsilon - \epsilon_c)^2$$ ........................ (5)

$$R_{i,m} = \frac{k_1 P_i (\chi_i - \chi_0) C_i}{1 + P_i \chi_i / k_2}$$ ........................ (6)

Where $P_i$ is the pressure of gas and $C_i$ is the density of $i$th gas. According to Takatani et al.,31) it has been known that $k_1$ becomes approximately the same value regardless of the coke reactivity and it is controlled by CO restraint term $k_2$ from the similar experiment (CRI=30.6–39.4). Based on this result, it is supposed that $k_1$ is constant, $k_1 (1/\text{atm} \cdot \text{s}) = 2.7 \times 10^6 \exp(-60400/RgT)$, assuming $k_2$ and closed pore $\epsilon_c$ as a parameter and it is specified by the fitting from the experimental result.

3.1.2. Experimental Result

Figure 4(a) shows the reaction rate transition measured from load cell, for samples of CO2 (CRI=28.6) and C10 (CRI=44.4). The lines are calculated value after the parameter optimization ($k_2$, $\epsilon_c$). Also, Fig. 4(b) shows the reaction rate distribution from EPMA and the same optimization calculated. As well known generally, if the pore structures are same when the coke reactivity increases, the reaction would be generated in the approach surface side, but in the case in which initial porosity is high, or $-10 \mu m$ size porosity is low, the reaction progresses to the inside were also seen.

Figure 5(a) is Arrhenius plot of $k_2$ which was calculated by each coke with different CRI values from the experimental result. The result (CRI=30.6, 34.0, 39.4%) of Takatani et al.31) was shown together in the figure. Effect of CRI on activation energies $E_{k_2}$ and frequency-factor $A_{k_2}$ was shown in Fig. 5(b). Both have good correlation and the regression formulas of CRI were obtained by

$$A_{k_2} = 60.9 \exp(-0.0901 \text{CRI})$$ ........................ (7)

$$E_{k_2} = 96.5 \exp(-0.0372 \text{CRI})$$ ........................ (8)

Figure 6(a) shows the relation of optimized parameter $\epsilon_c$ and $-10 \mu m$ porosity measured by mercury porosimeter. It was found that both have correlation as follows

$$\epsilon_c = 1.14 \epsilon_{-10 \mu m} + 21.2$$ ........................ (9)

and involve in the closed pore that fine pore doesn’t affect a gas diffusion. The change of pore-size distribution in coke after the reaction is showed in Figs. 6(b), 6(c) measured by
mercury-porosimeter. It is found that the reaction has mainly been generated in the pore over 10 μm. Therefore, if CRI and –10 μm of porosity ε_{–10 μm} are measured, Eqs. (7)–(9) are fixed and from Eqs. (3)–(6) a coke gasification reactivity can be estimated.

Next, the gasification reaction start temperature will be discussed. Figure 7(a) shows the relation of reaction rate to temperature in Experiment 1. When the coke reactivity
increases, the reaction would start from the lower temperature. According to Experiment 3 result in Fig. 7(b), gasification rate exceeds reduction rate at the range of $1.3\times10^{-2}$ mol/min/each CRI. Those value are correspondent to $1.2\times10^{-3}$ min$^{-1}$ divided by reacted mole number. Therefore, it was assumed that standard rate of the gasification reaction start is $r_c=1.36\times10^{-3}$ min$^{-1}$ and the reaction temperature which was taken in Fig. 7(a) was shown in Fig. 8.

And the effect of the temperature on the difference in gasification reaction and reduction rate was taken in Fig. 7(b) was also shown in Fig. 8.

The calculated temperature at $r_c$, which is obtained, substituting $r_c$ and Eqs. (7)–(9) for Eq. (6) was described together in the figure. Following Fig. 8, the decline of the reaction temperature of thermal reserve zone in furnaces according to CRI can be estimated. To confirm this effect, the following Experiment 2 was carried out.

3.2. Effect of Coke Reactivity on Reduction Equilibrium (Experiment 2)

By giving the gas composition of CO–CO$_2$ system which is near the FeO–Fe reduction equilibrium Experiment 2, and a result of searching temperature of reduction equilibrium from exhaust gas is shown in Fig. 9. In equilibrium state, exhaust gas composition is equal to inlet gas composition. The highest temperature within the equilibrium temperature in Experiment 2 is correspondent to temperature of thermal reserve zone in blast furnaces that is gasification start temperature.

When obtaining equilibrium temperature from the gas composition by the reactivity change of the coke, with CRI=28.6(C02)$\rightarrow$45.1(C11), the equilibrium temperature declined by about 120°C. The reason why this temperature decrease range ($-73^\circ\text{C}/\text{CRI}+10\%$) was agreed with the inclination of Fig. 8 approximately is considered to be that reduction rate follows in the case of sinter JIS-RI=65.3 (S04) which was used even if the temperature declines with the CRI increase.\(^{12}\)

While Gaballah et al.\(^{35,36}\) pointed out a problem with lower reduction rate than gasification reaction rate when they used high-reactivity coke in the coupling reaction. The reason is considered that it is because reducibility of ore was low to the difference of coke reactivity. In case of this review, even if JIS-R1 is low comparatively (=65.3), reduction rate shows adequate to CRI 28.6$\rightarrow$45.1. Therefore, following Fig. 8, it supposes a blast furnace temperature profile change according to coke reactivity CRI and it shall be the condition of Experiment 3.

3.3. Effect of Coke Reactivity on High Temperature Property (Experiment 3)

3.3.1. Change of the Experimental Conditions According to the Coke Reactivity

The temperature increase and the inlet gas composition pattern of Experiment 3 was shown in Fig. 2. Changed to the low temperature side based on CRI increase of each coke was based on the result of Fig. 8, that is above mentioned temperature decrease range ($-73^\circ\text{C}/\text{CRI}+10\%$).

3.3.2. Evaluation Method for Reaction Rate

Coke gasification reaction rate $R_{i=\text{CO}_2}^{\text{sol}}$, where $i=\text{CO}_2$ was determined from Eqs. (3)–(9), and sinter-ore reduction rate $R_{j=\text{hematite}}^{\text{red}}$, where $i=\text{CO}$, $j=\text{hematite}$, magnetite, wüstite was determined from the unreacted core shrinking model. The overall reaction rate constant is represented by 1) mass transfer in a boundary film $k_m$ expressed as Nelson’s equation,\(^{32}\) 2) effective coefficient of diffusion $D_{ej}$ expressed from the molecular diffusion $D_{ij}$, and 3) reaction rate for each phase $k_j$. Here, the effect of JIS-R1 on $k_j$, and $D_{ej}$ was required so that the calculation result in the JIS-R1 experimental condition (fixed bed, 900°C) may agree with JIS-R1 value. So, the $k_j$ was determined like Fig. 10, and the similar estimations ever existed\(^{37,38}\) under various conditions was shown together in the figure. The packed bed in the graphite crucible is made to be fixed bed of height direction one dimension:z-axis, and the material balance of reactant gas is shown in the following equation.

$\varepsilon \frac{\partial C_i}{\partial t} + u \frac{\partial C_i}{\partial z} = d \int R_{i=\text{CO}_2}^{\text{sol}} dv + \sum_{j=1} v_d R_{j=\text{hematite}}^{\text{red}} \quad \ldots \quad (10)$
The solid side of the right-hand side can be expressed through the reaction rate of coke and ore included CRI, JIS-RI each placed in the height direction of bed. The initial condition:
\[ t=0: R_{i,j}(0,z)=0, \]
and boundary condition:
\[ z=0: C_i(0,t)=C_i(z=0) \]
were set it, and the time change of temperature in proportion to the experimental condition and gas composition was input, assuming that the temperature in packed bed was constant.

### 3.3.3. Result: Behavior of Soften-melting and \( R_{re} \)

The experimental result in using S07 and C03 is shown in Fig. 11. At 1200°C, after the inlet CO stops, by the reduction reaction, CO occurs for a while, beyond the vicinity of 1300°C which pressure-drop became max, the CO\(_2\) declines and it approaches the zero. Also, the CO generation rate stagnate at around 1350°C, and changing to the decrease, when approaching a dripping temperature about 1500°C, the melting reduction by slag FeO and carburization becomes active, the exhaust CO increase rapidly, the exhaust gas flow rate increase and the specimen temperature declines, and metal dripping begins soon. It is considered that this rapid melting reduction and carburization is caused by generating a new reaction phase surface with the coke by the flow start of melted FeO of immediate before the dripping. Therefore, the gas reduction completion temperature assumed CO\(_2\) occurrence stop=CO/CO\(_2\) increase stagnation timing. Thus, the reduction degree \( R_{red} \) as \( T=T_{re} \) is defined as final indirect reduction degree; \( R_{re} \) as follows.

\[
\frac{\partial}{\partial T} (CO/CO_2)_{exhaust} \bigg|_{T=T_{re},T=2000°C} = 0, R_{re} (T = T_{re}) \leq R_{red} (T = T_{re})
\]

In order to confirm the behavior of shrinking and melting, interrupting in increasing the temperature in each step, after N\(_2\) cooling separating welded or fused materials in the slag and metal, and each chemical analysis was performed. The cross section photograph of each step in the crucible, and the vertical variation of calculated reaction degree are shown in Fig. 12. The photograph shows that the sinter in two layers behaves in almost similar manner for welding until immediate before dripping inside of the crucible. In case of 1200°C stopping, reduction degree reaches to 68.3% (T.Fe/FeO/M.Fe=65.1/25.7/38.4) and approximately agrees with reduction degree curve in Fig. 11. From shrinkage ratio becomes 30–40% around 1200°C, until it becomes 50% at around 1250°C, it is rapid shrinking region. In this temperature, the void in the sinter bed almost disappears by the softening weld, also, because the wüstite rich unreacting nucleus exists inside a particle and the perimeter part is covered with metallic shell, it is estimated that this is a declining factor for the reaction rate. At this point around 1250°C, concentration estimated with about 20–30% FeO melt is formed inside a particle and the reduction degree is calculated 70%. At immediately before 1295°C where it reaches a maximum pressure-drop, welding among particles is progressing. Observed reduction degree of the fusion ore in this point is 67.8% (T.Fe/FeO/M.Fe=76.1/30.2/45.2), and it is almost near for 72% of the calculated value. The reduction degree is 89.7% (T.Fe/FeO/M.Fe=79.8/5.2/70.5) when it becomes 1500°C of the dripping temperature, and it agrees with the calculated reduction degree of the gas balance.

Coke reaction rate in Fig. 11 was calculated from the measurement of coke weight loss after reaction: \( R_c \) and the calculated values show the reacting weight by gasification reaction only. The difference of the weight decrease which is recognized in both is 6–8% and it was found while it is considered to be the reaction which the coke was affected except gasification, i.e. the FeO melting reduction, the carburization, the ash evaporation and so on in chapter 3.3.5 (Fig. 17). It is considered that \( R_c \) is the important index which affects coke strength after reaction in the blast furnace lower.\(^{22}\)

### 3.3.4. Result: Reaction Degree

Figure 13 shows reaction rate and the displacement curve. The reduction degree clearly rises from low temperature area (<1000°C) in high JIS-RI. However, according to
Fig. 12. Cross section photograph and vertical distribution of reaction degree in the crucible. a) Calculated vertical distribution of reduction and gasification degree at 900°C, 1050°C, 1200°C and 1350°C simulated experiment 3. b) Cross section of quenched and filled by resin at 1200°C, 1295°C, 1500°C, and after Experiment 3 (R: Reduction degree, ΔP: Pressure drop).

Fig. 13. Reaction degree and shrinkage (Experiment 3).

Fig. 14. Effect of JIS-RI and ΔKS on final indirect reduction degree $R_{re}$ (Experiment 3). a) Relation between $R_{re}$ and JIS-RI (correlation coefficient $R^2 = 0.0755$). b) Relation between $R_{re}$ and $\Delta KS$ (correlation coefficient $R^2 = 0.292$).

Fig. 15. Shrinkage, permeability and C in iron in softening-melting process. a) Shrinkage and permeable resistance K. b) Carbon in metallic iron in softening-melting (Experiment 3: S07/C03, Experimental blast furnace, 39,40). S02, S03/ C01, 03).

Fig. 14, when JIS-RI is high, the final indirect reduction degree $R_{re}$ is almost high but some fluctuation exists for example S03 is exception. Also, $R_{re}$ tends to rise when $\Delta KS$ is small. Therefore, even when JIS-RI is low, if $\Delta KS$ is low, $R_{re}$ can be maintained high and $KS$ also can be kept at low level. Further, replacing coke with high CRI, the gasification rate and the reduction degree near 900°C rise as shown in Figs. 13, 14. Also, $R_{re}$ increase and the coke final reaction degree $R_{c}$ declines.

3.3.5. Result: Softening-melting Property

Figure 15 shows shrinkage and permeable resistance index K over 1100°C (a) and carbon content in iron part after quench (Fig. 12) and in dripped iron (b). $KS$ decrement by using high CRI and high JIS-RI is recognized in the rise of $R_{re}$ and shrinkage start temperature ($T_s$) and dripping start temperature ($T_d$) range narrows by high CRI coke as well correspondent to cohesive zone width being thin. When coke CRI is high, the packed bed is difficult to be shrunk, so that the temperature in which the shrinkage reaches 50%
is higher than low CRI case. By the decease in gasification start temperature, the reduction degree increase and residual FeO lowers.

So the shrinkage of the packed bed is suppressed through the lowering of melt quantity and \( KS \) may decrease. And, when residual FeO lowers, the carburization is promoted, so that the metal dripped temperature (\( T_{\text{drip}} \)) seems to lower in high CRI coke, but from Fig. 15(a), \( T_{\text{drip}} \) is dependent on sinter regardless of the coke. \( T_{\text{drip}} \) in case of using S11 (CaO/SiO\(_2\)=1.84) is lower than in case of S07 (CaO/SiO\(_2\)=2.00). Because the carbon content in metallic iron rises at the initial stage of shrinkage, the carburization has been started in this stage (1 200–1 300°C), and it is possible to interpret that metallic iron dripping after iron melt which increases by the smelting reduction afterwards (1 450–1 500°C) sufficiently absorbed C necessary for separate slag and metal as influencing the slag composition of sinter derivation further than residual FeO (Fig. 15(b)).

**Figure 16** shows the effect which coke CRI exerts on the behavior in the the softening shrinkage.

Softening viscosity\(^4,41\) (Mpa·sec) is defined at the value which divided the load (Mpa) by the shrinkage rate (%/sec) at first half shrinkage (10–50%) and latter half (50–100%) respectively \( \eta_{10/50} \), \( \eta_{50/E} \).

There were increase of \( \eta_{10/50} \) and lowering of \( KS \) by the increase in CRI. It shows that the reduction is promoted at the low temperature near the coke gasification starting temperature and that the early stage softening shrinkage resistance rises.

Figure 17(a) shows the effect of the CRI exerts on \( R_{\text{re}} \) or on the coke reaction rate, and Fig. 17(b) shows for comparison when a rising temperature pattern is assumed to be constant even if the coke CRI is changed in the experiment 2.

Also, a calculation result by the reaction model was shown in the figure respectively. The increase range of \( R_{\text{re}} \) by the CRI rise of Fig. 17(a) which heat pattern was changed according to the reactivity is bigger than that of Fig. 17(b). This is because that for Fig. 17(b) the \( R_{\text{re}} \) rose with the increase of the gasification reaction weight by the CRI rise whereas for Fig. 17(a) the reduction became active from the low temperature by the CRI rise and the heat pattern change. It can be evaluated with that Fig. 17(a) is closer to the real blast furnace condition, since gasification reaction is not dependent on CRI. As mentioned above, it is proven that the weight loss \( \Delta \) difference calculation and observation 6–8% which melting reduction, carburization, ash content evaporation, etc. does not depend on CRI.

3.3.6. Relation between Final Reduction Degree and High Temperature Permeable Resistance

**Figure 18** shows relation between \( R_{\text{re}} \) and \( KS \). As for the

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**Fig. 16.** Effect of CRI on softening viscosity and \( KS \). a) \( \eta_{10/50} \): Softening viscosity at 10% shrink to 50%, \( \eta_{50/E} \): Softening viscosity at 50% shrink to shrink completion. b) \( KS \) of vertical axis is the result of Experiment 3. \( \Delta KS \) of caption is estimated in chemical content.

**Fig. 17.** Effect of CRI on reaction degree \( R_{\text{re}} \), \( R_{c} \). a) Temperature pattern changed by CRI correspondent to blast furnace operation. b) Temperature pattern constant.

**Fig. 18.** Effect of indirect reduction \( R_{\text{re}} \) on permeability from simultaneous evaluation of sinter and coke by softening-melting test.
ity changes of the sinter and the coke.

There-fore, it is considered that $R_{\text{sinter}}$ is high and $KS$ is low. However, even if JIS-RI is 65% or less, when MgO was high comparatively, some cases existed where $R_{\text{sinter}}$ was high and $KS$ was low (S03). Also, by the CRI rise of the coexisting coke, through the rise of $R_{\text{sinter}}$, $KS$ decrease. According to this study result, it found that the rise of $R_{\text{sinter}}$ and the decrease of $KS$ had a similar inclination approximately in both cases. Therefore, it is considered that $KS$ is affected most by the reduction degree which is eventually obtained by various reactivity changes of the sinter and the coke.

4. Conclusion

Softening-melting test which simulated the temperature profile in blast furnaces determined by the reactivity of coke was carried out. And it was shown that this method is effective for simultaneous estimation of carbonaceous and ferrous burdens to cohesive zone of blast furnaces. The effect of coke and sinter reactivity on sinter soften-melting property at lower part of blast furnaces was evaluated, and following results were obtained.

1) Lowering of coke gasification start temperature by increase in coke CRI makes FeO-Fe equilibrium point move to the lower temperature direction. When coke CRI increases by 1%, the temperature of thermal reserve zone decrease 7.5°C.

2) The total gas reduction of sinter finishes at temperatures between 1300 and 1400°C. The final indirect reduction degree of sinter $R_{\text{sinter}}$ is 80–95%.

3) When coke reactivity increases, reduction rate of sinter at 900–1000°C increases through the lowering the temperature of gasification start. As a result, softening viscosity at first half shrinkage near 1200°C, increase, and the high-temperature permeable resistance index $KS$ decreases.

4) The high-temperature permeable resistance $KS$ value decreases, when the final reduction degree of sinter is increased by coke CRI, sinter RI or sinter composition.

REFERENCES

38) Y. Iwanaga: (1990) private communication.