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1. Introduction

1.1. Feature of metallurgical coke and the role in blast furnace

Metallurgical coke is made from coal that is an organic compound, but is inorganic material composed of graphite. Metallurgical coke is porous media that contains pore of 50% in porosity. The size of metallurgical coke lump is from 25 mm to 50 mm (Fig. 1). In modern iron making process, coke has very important roles in iron making process because coke is, at the same time, used as reducing agent of ore, heat source of blast furnace, carburizing source of pig iron and spacer of gas and liquid transport through blast furnace. Metallurgical coke is charged from the top of blast furnace at first and moves to the bottom part. Reducing agents derived from coke are generated by following two reactions: (i) coke reacts with oxygen at the bottom part of blast furnace, and one carbon monoxide molecule is generated, (ii) coke reacts with carbon dioxide at middle part of blast furnace, and two carbon monoxide molecules is generated. Former reaction is combustion and latter reaction is named carbon (or coke) solution-loss reaction. Firstly, carbon monoxide generated from combustion reaction reduces ore (FeOx) and becomes carbon dioxide. Then, carbon dioxide reacts with coke and two carbon monoxide molecules is generated.

1.2. Social background

Blast furnace operation consumes huge amount of carbon that finally becomes carbon dioxide. In recent years, worldwide, iron making materials (i.e. coal) are draining and soaring. So, improvement of carbon use efficiency to curtail carbon consumption is increasingly important issue from the viewpoint of material, energy resource and cost.
Combustion of coke takes the role of primary carbon monoxide generation. So, this gasification reaction is carbon consumption reaction. Carbon solution-loss reaction, also, consumes carbon, but is, on the other hand, gasified carbon recycle reaction (from carbon dioxide to carbon monoxide). Reactivity of these gasification reactions directly affects carbon use efficiency of iron making process. Gasified carbon produced by combustion reaction is finally emitted as carbon dioxide due to oxidization reaction of ore. Thus, control of coke solution-loss reactivity is important in order to improve of the carbon use efficiency. Both practical approaches and fundamental investigation are desired to this.

![A photograph of coke lump](image1)

(a) A photograph of coke lump

![Cross-sectional image of coke microstructure](image2)

(b) Cross-sectional image of coke microstructure

**Figure 1.** Photographs of (a) coke lump and (b) cross-sectional image of coke microstructure

1.3. Purpose and outline of this chapter

As above, promoting and controlling solution-reactivity of metallurgical coke is very important in order to improve the carbon use efficiency. To realize the blast furnace operation in high carbon use efficiency, making of the coke which is satisfying four roles described in 1.1 and is solution-loss reactivity-promoted is required.

The practical purpose of the chapter is to propose the design guide of solution-loss reactivity-promoted (so-called “highly reactive”) coke from the viewpoint of use in blast furnace. There are many conditions (e.g. thermal, chemical or mechanical condition) which affect descending and reacting metallurgical coke in blast furnace. For this, the proper metallurgical coke should be made with considering the effects of these conditions. The chapter, hence, focuses on the fundamental knowledge and research about metallurgical coke gasification in the effect of thermal, chemical and mechanical condition. At first, the situation in blast furnace and the role of coke gasification reactions in blast furnace are introduced in section 2. The effect of catalyst, as useful way to promote the solution-loss reactivity, on solution-loss reactivity is discussed in section 3. Then, in section 4, the problem
from the viewpoint of the strength caused by promotion of solution-loss reactivity is noted, and the phenomena of highly reactive and normal coke are investigated in order to provide the solution of the issue. To discuss about both of the reactivity and the strength of highly reactive coke, the reaction mechanism and phenomena of highly reactive coke before and after the gasification reaction is investigated in this section. Furthermore, we propose a proper method to make highly reactive coke catalyzed by metals.

2. Situation in blast furnace and role of metallurgical coke gasification

Situation in blast furnace and role of coke gasification can be discussed from two viewpoints. One is chemical reaction and thermodynamic equilibrium state. Metallurgical coke is gasified with oxidation product such as carbon dioxide, and reductive gas such as carbon monoxide is generated. In blast furnace, any fraction of the components is governed by thermodynamic equilibrium state in C-O-Fe system and reaction kinetics caused by the difference between actual and equilibrium state. The other is the effect of coke solution-loss reactivity on carbon use efficiency in blast furnace. Using coke with high solution-loss reactivity, equilibrium state changes because solution-loss reaction is endothermic and the temperature at TRZ decreases. As a result, necessary quantity of carbon (coke) decreases.

2.1. Chemical reaction and the thermodynamic equilibrium state in C-O-Fe system (Bannya, 2000)

2.1.1. Combustion (reducing gas generation)

In blast furnace, carbon atom of coke reacts with oxygen molecule from tuyere

\[
\begin{align*}
C(s) + O_2(g) & = CO_2(g) \\
\Delta H_{298}^o & = -393.5 \text{ kJ/mol} \\
\Delta G_{298}^o & = -393500 - 2.99T \text{ J/mol},
\end{align*}
\]

where \(\Delta H_{298}^o\) is standard enthalpy change of formation, \(\Delta G_{298}^o\) is standard free energy and \(T\) is absolute temperature. Generated carbon dioxide by reaction of Eq. (1) reacts because there is much solid carbon as coke,

\[
\begin{align*}
C(s) + CO_2(g) & = 2CO(g) \\
\Delta H_{298}^o & = 172.4 \text{ kJ/mol} \\
\Delta G_{298}^o & = -171660 - 175.02T \text{ J/mol}.
\end{align*}
\]

As a result, following reaction occurs near the bottom part of blast furnace

\[
\begin{align*}
2C(s) + O_2(g) & = 2CO(g) \\
\Delta H_{298}^o & = -221.1 \text{ kJ/mol} \\
\Delta G_{298}^o & = -221840 - 178.0T \text{ J/mol}.
\end{align*}
\]
Reaction of Eq. (3) is called combustion of coke. Two molecules in carbon monoxide as reducing gas and 221.1 kJ in thermal energy is generated by reaction of Eq. (3) with one molecule in \( \text{O}_2 \). Temperature near the tuyere of blast furnace is 2570 K that is similar to adiabatic flame temperature of reaction of Eq. (3).

2.1.2. Iron oxide reduction

Reducing reaction of iron ore (oxide) in blast furnace is classified into two kind of reaction. One is indirect reducing reaction with carbon monoxide. The other is direct reducing reaction with solid carbon. “Direct” or “indirect” is called whether solid coke is directly gasified. Indirect reaction occurs at the top or middle part of blast furnace and direct reaction progresses at the bottom part. Indirect reducing reaction is written in

\[
\text{FeO}_m (s) + \text{CO(g)} \rightarrow \text{FeO}_{m-x} + \text{CO}_2(g). \tag{4}
\]

This successive reaction is a desirable reaction from the viewpoint of the thermal balance in blast furnace because the reaction is an exothermic except reducing reaction from magnetite to wustite. Direct reducing reaction, on the other hand, is written as follows:

\[
\text{FeO}_m (s) + m\text{C(s)} \rightarrow \text{Fe} + m\text{CO(g)}. \tag{5}
\]

Reaction of Eq. (5) progresses at the bottom part of blast furnace where combustion of coke occurs and is endothermic. It negatively affects the amount of energy consumption that reaction of Eq. (5) mainly occurs. To improve carbon use efficiency (thermal efficiency), it is important to enhance indirect reducing reaction because reducing ratio of iron ore by indirect reducing reaction should be lifted rather than that of direct reducing reaction.

2.1.3. Coke solution-loss reaction

Reaction of Eq. (2) can be also expressed as equilibrium reaction.

\[
\text{C(s)} + \text{CO}_2(g) = 2\text{CO(g)}
\]

\[
\log K_p = -8696 / T + 9.14 \tag{6}
\]

where \( K_p \) is equilibrium constant. Equilibrium of Eq. (6) is called Boudouard equilibrium. The composition of this equilibrium relates with reaction of Eqs. (1)-(5), and dominates state of C-O-Fe system (e.g. composition of Fe\(_2\)O\(_3\), Fe\(_3\)O\(_4\), FeO, Fe, CO\(_2\), CO, C and so on) in blast furnace. The reaction toward right hand of Eq. (6) is endothermic and is promoted with high temperature. At the bottom part of blast furnace where the temperature indicates 2570 K, ratio of CO/(CO+CO\(_2\)) is almost 1.0. At the middle part of blast furnace, the ratio is about 0.9. This reaction at the middle part of blast furnace is, in particular, called carbon solution-loss reaction.
2.2. The effect of coke solution-loss reactivity on carbon use efficiency

2.2.1. Thermal reserve zone

Figure 2 shows conceptual diagram of temperature distribution along the height direction in blast furnace. TRZ (Thermal Reserve Zone) is where temperature slightly changes over the cohesive zone. In TRZ, indirect reducing reaction actively progresses rather than direct one. The degree of progress of indirect reducing is affected by TRZ temperature because the temperature governs state of C-O-Fe equilibrium system in TRZ. Coke solution-loss reaction, also, occurs in TRZ and its reactivity strongly affects TRZ temperature. TRZ temperature decreases when solution-loss reactivity of charged coke is enhanced due to endothermic reaction. Therefore, coke with high solution-loss reactivity is used in blast furnace, and TRZ temperature decreases and the equilibrium point moves. However, final conversion of coke gasification (ratio of weight loss based on carbon) is constantly 20 mass% regardless of gasification reactivity.

Figure 2. A conceptual diagram of temperature distribution along height direction of blast furnace

2.2.2. Rist diagram

Rist et al. proposed the model that represents a state of blast furnace operation based on thermal and chemical equilibrium state (Rist & Bonnivard, 1962; Rist & Meyerson, 1967). The both equilibrium states at temperature of TRZ and tuyere are plotted (Rist diagram), and the state of the operation (e.g. carbon use efficiency C/Fe that is amount of carbon use per unit reduced iron) can be estimated. Rist diagram is convenient tool to describe the effect of coke solution-loss reactivity on carbon use efficiency. Figure 3 shows an example of Rist diagram with the operation line. Horizontal and vertical axes show O/C and O/Fe, respectively. State of C-O-Fe equilibrium system can be understood in blast furnace. Gas equilibrium in C-O system at tuyere is shown in the lower left part of cut Rist diagram into quarters, state of C-O-Fe equilibrium system in TRZ is represented in the upper right part of the cut diagram, and state of iron oxide in O-Fe system is indicated in the lower right part of the cut diagram. Gradient of the line in Rist diagram means carbon use efficiency C/Fe = (O/C)/(O/Fe) . The “W” point shows ideal operation state that is in equilibrium state in TRZ.
If TRZ temperature decreases with enhancement of coke reactivity, gas equilibrium of C-O-Fe system is shifted to oxygen state (a decrease in ratio of CO/CO₂ in equilibrium). Then, the new “W” point is plotted in Rist diagram. Indirect reaction of Eq. (4) is promoted because carbon dioxide generation is promoted due to the new equilibrium that indicates oxidation atmosphere. As a result, the carbon consumption for thermal conservation at the bottom part of blast furnace is curtailed because the amount of reducing iron caused by direct reducing that adsorbs the heat decreases (Ariyama et al., 2005; Ariyama, 2009; Naito et al., 2001). It means that carbon use efficiency C/Fe can be improved. There is some actual proof of this improvement using BIS (blast furnace inner-reaction simulator) (Naito et al., 2001) and commercial blast furnace (Nomura et al., 2005).

**Figure 3.** An example of Rist diagram with the operation line

### 3. The effect of catalyst on solution-loss reactivity

Reaction gas of coke solution-loss reaction (carbon dioxide) adsorbs and/or chemisorbs on the site of graphite structure. It is expected to be able to enhance the reactivity by a change of the site state. It is, however, difficult to change the site state by a change of only coke making process. Another idea is addition of metallic catalyst. This section will discuss about the element that indicates the catalyst activity, the effect of element and state of catalyst on solution-loss reactivity, and additional method.

The catalyst activity in each element have been organized and is shown in Fig. 4 (Lahaye & Ehrburger, 1991). Many kinds of alkali metal (Lahaye & Ehrburger, 1991; Tomita et al., 1983; Walker, 1968; Miura et al, 1989; Takarada et al., 1992; Jaran & Rao, 1978), alkaline earth metal (Tomita et al., 1983; Miura et al, 1989; Sears et al., 1980; Carzorla-Amoros et al., 1992; Yamada & Homma, 1979) and transition metal (Ohtsuka et al., 1986; Kashiwaya et al., 1991;
Tomita et al., 1983; Kamishita et al., 1980) shows good catalyst activity. Many kinds of inexpensive metal show the activity such as potassium, calcium and iron, respectively.

In metallurgical coke, on the other hand, there is mineral that is derived from coal ash and has catalyst activity. In addition, coke-matrix is not perfect graphite structure and amorphous structure coexists with crystalline structure. Therefore, it is necessary to consider the effect of the catalyst on solution-loss reactivity of metallurgical coke. Nomura et al. have compared catalyst activity among different element and compound (Nomura et al., 2005). Strontium, calcium and magnesium were selected. Figure 5 shows the relationship between the addition ratio of the alkaline earth metal and the JIS coke reactivity index. Rank of catalytic activity is Sr > Ca >> Mg. However, in this examination, they selected calcium as catalyst from these candidate materials because of cost performance of each material. In addition, he has reported that there is little difference between oxidation metal and carbonate. Grigore et al. have reported that not all iron, calcium, potassium and sodium crystalline mineral phases present in the coke catalyse the gasification reaction (Grigore et al., 2006). Coke reactivity increased with increasing total amount of catalysts in the crystalline phases. They concluded that the most likely materials responsible for the variation in coke reactivity are metallic iron and iron sulfides with a possible contribution by iron oxides and calcium sulfide. Kashiwaya et al. have particularly examined the reaction mechanism of solution-loss reaction with iron catalyst (Kashiwaya et al., 1991). Metallurgical coke, graphite and these materials with iron catalyst were gasified. The effect of iron addition to graphite is stronger than that to coke because of original mineral in raw coal. There are two ad- and/or chemisorption site on coke. First one is adsorbed by carbon dioxide and second one is adsorbed by carbon monoxide. If latter one increases with addition of iron catalyst, carbon dioxide adsorption is competitively inhibited and gasification rate decreases rapidly. It seems that adding iron to coke, latter site decreases and gasification is catalyzed.

Figure 4. The catalyst activities in each element (Lahaye & Ehrburger, 1991)
As above, it seems that iron is the most useful source of catalyst because of cost, catalyst activity and source of pig-iron. Useful source of catalyst second to iron seems calcium, also, is very economical material but melt in by-product as slag.

Catalyst addition method can be classified into pre- and post-addition (Nomura et al., 2005). Pre- or post- mean before or after coke making. Figure 6 (Nomura et al., 2005) shows conceptual diagrams of both methods of catalyst addition. Post-addition is easier to enhance solution-loss reactivity (Kitaguchi et al., 2007) and to control the type of reaction and reaction surface than pre-addition (Nomura et al., 2007). On the other hand, process of pre-addition is simpler than that of post-addition, and is employed in extensive examination.
(Nomura et al., 2005; Nomura et al., 2006; Nomura et al., 2007; Nomura et al., 2009; Fujimoto & Sato, 2010; Yamamoto et al., 2011; Yamazaki et al., 2010; Yamazaki et al., 2011). Particularly, if Fe addition is used, iron ore as iron/steel making material is useful as the source of catalyst (Nomura et al., 2009; Fujimoto & Sato, 2010; Yamazaki et al., 2010). Iron ore in briquetted material before carbonization (mixed-coal/ore = 70/30) is almost reduced during carbonization (reducing ratio is ca. 95%, Fujimoto & Sato, 2010).

4. Reaction type of metallurgical coke lump during solution-loss reaction with and without catalyst – The phenomena of coke-matrix state and controlling process in the lump

4.1. Introduction

4.1.1. The strength after gasification reaction and the spatial distribution of local porosity in coke lump

For the improvement of the carbon use efficiency, the important factors of highly reactive coke are not only the gasification reactivity of metallurgical coke but also the strength of one because metallurgical coke supports gas and liquid permeability in blast furnace. The issues on the strength of highly reactive coke are principally caused by catalyst addition. The issues can be divided into two main classes.

As the first one, at the time of before changing into blast furnace, coke strength changes (or mostly decreases) with catalyst addition regardless of adding method. Studies of coke strength degradation with catalyst addition have been performed (Nomura et al., 2005; Nomura et al., 2009; Fujimoto & Sato, 2010; Yamazaki et al., 2010). There are studies and knowledge in order to clarify mechanism of strength development or strength degradation as well as reports for practical and commercial making method. The cause of the strength degradation is the inhibition coal particle swelling and adhesion each other. A certain level of knowledge and technology is developed, and the coke that has appropriate strength before charging into blast furnace can be made now.

As another one, after charging into blast furnace and after gasification reaction, coke strength of highly reactive coke changes from that of non-reactivity-promoted coke. It is considered that coke pulverization and coke breeze generation are promoted after the gasification reaction because coke-matrix is more vanished and embrittled when the gasification reaction is catalyzed. Porosity or local porosity of porous media (rather than matrix strength of porous media strongly) affects its strength; hence a change of porosity or local porosity due to the coke-matrix vanishing. As practical knowledge, spatial distribution of local porosity of coke lump after gasification reaction strongly affects the strength of gasified coke (Kamijo et al., 1987). Nishi et al. have reported that coke after gasification has high pulverization resistance when there is unreacted-core observed as spatial distribution of local porosity of coke lump (Nishi et al., 1984; Nishi et al., 1987). Watakabe et al. have reported that the coke whose spatial gradient of gasification ratio (local porosity) near the outer region of coke lump is sharp has high pulverization and fracture resistance (Watakabe et al., 2001).
There are few fundamental (i.e. phenomenon analysing based) studies of a change of coke strength after gasification reaction (e.g. causal correlation between gasification reaction and the strength from the viewpoint of transport phenomena and reaction mechanism) although there are some reports in practical test. Meanwhile, it is certain that the coke has high pulverization resistance, if there is “unreacted-core” in spatial distribution of local porosity from empirical fact. It is because that the coke is planed from outer region with marked embrittlement, but fracture hardly occurs due to strength-reserved core. Hence, the fundamental studies should be used to develop the “unreacted-core” in spatial distribution of local porosity.

4.1.2. Reaction type of coke lump (resistance of reaction gas consumption in the lump and resistance of reaction gas diffusion into coke lump of as reaction-controlling process of coke lump) – a factor of the spatial distribution–

The spatial distribution of local porosity of coke lump is as a result of (1) reaction gas diffusion into coke lump, (2) reaction gas diffusion in coke lump, and (3) gasification reaction of carbon(coke)-matrix. In other words, the resistance of (1), (2), and (3) dominate the spatial distribution. Resistance of (2) and (3) govern resistance of reaction gas consumption in the lump and resistance of (1) governs resistance of reaction gas diffusion into coke lump. Reaction type of coke lump, which is represented as homogeneous reaction model or unreacted-core model discussed in reaction engineering, seems to be a result of balance of both the resistances (reaction gas consumption in the lump and reaction gas diffusion into coke lump). If diffusivity of reaction gas into inner region of the lump is more dominant than gasification reaction of carbon material, homogeneous reaction may be observed (resistance of gas diffusion into the lump >> resistance of gas consumption in the lump). Meanwhile, if the gasification is more dominant than the diffusivity, unreacted-core remains and embrittlement may be selectively observed from outer region of coke lump (resistance of gas consumption in the lump >> resistance of gas diffusion into the lump).

4.1.3. Coke-matrix state – another factor of the spatial distribution

However, metallurgical coke is porous media that contains pore of 50% in porosity. The size of metallurgical coke lump is from 25 mm to 50 mm. Hence, the important factors that dominate the spatial distribution are not only the reaction type of coke lump but also coke-matrix state as a result of above processes (2) and (3). Although resistance of (1) overcomes other resistances in whole process, the each rate of the processes (2) and (3) is finite after reaction gas diffusion into coke lump.

As a result of these phenomena, coke-matrix state, after gasification reaction, changes of coke microstructure in mm-scale have been observed as follows: (i) Coke-matrix (solid) is visually vanished (Watakabe & Takeda, 2001; Hayashizaki et al., 2009) and is as change of local porosity, and (ii) Elastic modulus of coke-matrix decreases (Hayashizaki et al., 2009). In former phenomenon (i), carbon dioxide diffuses into coke-matrix insufficiently, and coke-matrix on the surface reacts. In latter phenomenon (ii), a decrease of elastic modulus of coke-
matrix is, on the other hand, correlated with nm-order micro pore volume. Hayashizaki et al.
reported the relationship between a decrease in the elastic modulus and an increase in nm-
order pore volume during chemical reaction-controlling condition in which gasification rate
of coke lump is not affected by reaction gas diffusion around the coke lump (Fig. 7, Hayashizaki et al., 2009). It has been known that volume of nm-order micro pore inside
coke-matrix increases with progress of gasification (Kawakami et al., 2004) because carbon
dioxide diffuses well into carbon-matrix.

Figure 7. Change in micro pore size distribution of metallurgical coke with conversion correlated with
elastic modulus by gas adsorption (Hayashizaki et al., 2009)

4.1.4. Purpose

If highly reactive coke reaction-promoted by catalyst is gasified, resistance of (3) decreases
when both reaction temperature of highly reactive coke and ordinary coke is the same;
hence the spatial distribution should become “unreacted-core”. Actually, reaction
temperature (i.e. TRZ temperature), however, decreases with use of highly reactive coke
described as section 2.2.2. Additionally, Gasification reaction may be promoted on surface of
the catalyst particle and coke-matrix. By existence of catalyst particle in coke lump, highly
reactive coke will show different reaction type of coke lump and coke-matrix state from non-
reactivity-promoted coke.

For this, as fundamental study, we have investigated the reaction mechanism and
phenomena of coke before and after the gasification reaction. In section 4, we detail and
discuss about these. The section is based on the research about these (Yamazaki et al., 2010;
Yamazaki et al., 2011). Figure 8 shows position of the study in this section and whole picture
of causal correlation between "coke gasification reaction" and "strength after gasification"
with condition, phenomena and mechanism. At first, actual spatial distribution of local
porosity of highly reactive coke in the TRZ condition when highly reactive coke is used in
blast furnace is examined. Next, the factors that govern the spatial distribution (reaction type
of coke lump and coke-matrix state) are estimated. Reaction mechanism estimation method is
used to estimate the controlling process. Nano indentation method is used to measure the
elastic modulus of coke-matrix. The elastic modulus is correlated with nm-order micro pore volume (Hayashizaki et al., 2009) that increases with progress of gasification (Kawakami et al., 2004).

Then, we propose a proper method to make highly reactive coke catalyzed by metals.

**Figure 8.** Position of the study in section 4 and whole picture of causal correlation between “coke gasification reaction” and “strength after gasification” with condition, phenomena and mechanism

### 4.2. Sample

#### 4.2.1. Making

Coke lumps with and without iron-particles were made. Both cokes are called ferrous coke and formed coke, respectively. Slightly-caking coal and non-caking coal were used. Table 1 shows proximate and ultimate analysis of coals. Iron ore is, also, used as the source of iron catalyst. Table 2 shows major component of iron ore. Blending ratio of slightly-caking and non-caking coals whose diameter was less than 3 mm was 70/30 based on mass. Both coals were mixed well. In making of ferrous coke, mixed coal was also mixed with 30 mass% of iron ore whose diameter was under 250 μm. Mixed material was pressed into 6 mL of briquette at 296 MPa and was carbonized at 1273 K for 6h. After carbonization, the blending...
iron ore was completely reduced to metallic iron and was distributed uniformly. A representative photograph of sample after carbonization is shown in Fig. 13. In appearance, there is little difference for formed and ferrous coke. Form of sample is briquette whose size is 29 mm x 24 mm x 21 mm. Above mixing, pressing and carbonization process is the same as previous studies (Fujimoto & Sato, 2010; Yamazaki

| Brand                  | Ash [db. %] | VM [db. %] | Fixed C [db. %] | Ultimate analysis [daf. %] |
|------------------------|-------------|------------|-----------------|----------------------------|
| Slightly-caking coal   | 8.4         | 36.1       | 55.5            | 82.3 5.8 1.9 0.88 9.1     |
| Non-caking coal        | 8.6         | 11.2       | 80.2            | 80.4 3.5 1.5 0.40 2.8     |

**Table 1.** Proximate and ultimate analysis of coals

| T-Fe | FeO  | SiO₂ | CaO | Al₂O₃ | MgO | P   |
|------|------|------|-----|-------|-----|-----|
| 67.5 | 0.21 | 1.31 | 0.01| 0.73  | 0.01| 0.033|

| S    | Na   | K   | TiO₂ | Mn   | Zn  |
|------|------|-----|------|------|-----|
| 0.010| 0.01 | 0.01| 0.07 | 0.11 | 0.003|

**Table 2.** Major component of iron ore [mass %]

4.2.2. Determination of loading mass% iron ore as Fe catalyst source

There are two purposes of Fe addition to metallurgical coke in iron/steel making process. First one is to decrease the amount of iron ore which must be reduced in blast furnace. Iron ore in briquetted material before carbonization (mixed-coal/ore = 70/30) is almost reduced during carbonization (reducing ratio is ca. 95%, Fujimoto & Sato, 2010). This fact shows that the required reducing gas that corresponds to carbon consumption to reduce iron ore can be decreased with the higher blending ratio of iron ore. Second one is to improve carbon use efficiency as described in section 2.2. Figure 9 shows that the initiation temperature of the gasification reaction decreases with an increase in the blending ratio of iron ore. The
initiation temperature strongly correlates with TRZ temperature described in section 2.2. The initiation temperature saturated at 30 mass% in the blending ratio. From these viewpoints, the higher blending ratio of iron ore is better. In fact, TRZ temperature satisfactorily decreases by using ferrous coke that includes 30 mass% in the blending ratio shown in Fig. 10 (No. 1 and No. 6 shows traditional metallurgical coke and ferrous coke, respectively, Nomura et al., 2009).

From the viewpoint of coke strength, the blending ratio of iron ore should be, on the other hand, limited. Figure 11 shows the relationship between the blending ratio of iron ore and tensile strength. Figure 12, also, shows relationship between the blending ratio of iron ore and agglomerated coal strength (the I-shaped drum index) that indicates pulverization resistance in blast furnace. By 30 mass% in the blending ratio, tensile strength and I-shaped drum index (ID600/10) are reserved, respectively. Both results suggest the same conclusion that the blending ratio of iron ore should be limited by 30 mass%. In Fig. 9, the effect of iron ore addition on TRZ temperature is satisfied at 30 mass% in the blending ratio. From the
both viewpoint of the carbon use improvement and the strength (Figs. 11 and 12), 30 mass% in the blending ratio is proper in practical use.

Adding 30 mass% of iron ore is, hence, proper in practical use.

![Figure 11. Relationship between tensile strength and blending ratio of iron ore (Yamazaki et al., 2010)](image1)

![Figure 12. The effect of blending ratio of iron ore on agglomerated coal strength (I-shaped drum index, ID600/10) (Fujimoto & Sato, 2010)](image2)

4.3. Gasification (solution-loss reaction)

4.3.1. Experiment

Ferrous coke lump and formed coke lump were gasified by carbon dioxide – carbon monoxide mixture gas. Schematic diagram of experimental apparatus is shown in Fig. 14. A coke sample was hanged from the weighing scale to alumina reaction tube filled with alumina ball for heat transfer to gas. Reaction tube was heated by electric furnace. Reaction gases were led into the reaction tube from the bottom. The gases after gasification were cooled by water-cooling tube, and were then ejected outside. Weight loss with the
Gasification reaction was measured by weighing scale. Experimental conditions are shown in Table 3. Reaction temperature was set at 1173 K. Reaction gas compositions were set at 100/0 (Yamazaki et al., 2010) and 50/50 (Yamazaki et al., 2011) in ratio of CO₂/CO. Final conversion (ratio of weight loss based on carbon) $x_b$ was 20 mass%.

Figure 13. A photograph of a sample after carbonization (in appearance, there is no difference for formed and ferrous coke) (Yamazaki et al., 2011)

Figure 14. Schematic diagram of experimental apparatus (Yamazaki et al., 2011)

4.3.2. Determination of reaction gas composition in this study compared with actual gas composition at TRZ

Main component of the actual gas at TRZ is N₂ besides CO and CO₂. The actual gas composition N₂/CO/CO₂ is ca. 60/20/20. N₂ is from air origin and is, however, inactive for the gasification reaction. In case of gasification reaction by the mixture CO/CO₂, the reaction rate is governed by $p_{CO}/p_{CO_2}$ when the reaction gas contains above 10% of CO, and the ratio of N₂ does not affect the gasification rate although the actual gas contains a massive amount of nitrogen. The reasons are as follows:
In the gasification reaction of solid-carbon by the mixture CO/CO₂, the reactions in series are analogous to the resistance in series. The reaction rate is controlled by the reaction step which exerts most of the resistance to the overall reaction. There are two rate-controlling mechanisms during the gasification reaction in series: (1) dissociation of CO₂ on the surface of carbon, and (2) formation of CO on the surface of carbon. Carbon monoxide has a two-fold poisoning effect: (a) covering of the surface site due to strong adsorption, and (b) increasing the activity coefficient of the activated complex for the dissociation of CO₂; hence CO changes the rate-controlling mechanism. In the gasification of carbon material (e.g. charcoal, graphite and metallurgical coke), at CO contents above 10%, resistance of (1) >> resistance of (2), and at low CO contents, resistance of (2) >> resistance of (1) (Turkdogan and Vinters, 1970).

In CO/CO₂ = 50/50, resistance (1) overcomes resistance (2). In this situation, the gasification rate is proportional to the difference of the partial pressure of actual gas CO₂ and the one governed by 2CO = C + CO₂ equilibrium. The equilibrium is determined as \( \frac{p_{\text{CO}}}{p_{\text{CO}_2}} \); thus the reaction rate is governed by actual gas \( \frac{p_{\text{CO}}}{p_{\text{CO}_2}} \) and equilibrium one. The actual gas composition indicated in the ratio of CO/CO₂ at TRZ is 50/50 (Nomura et al., 2006 and Nomura et al., 2009). So, the composition in the section, CO/CO₂ = 50/50, can represents the actual blast furnace condition, especially so-called at TRZ. Therefore, the results for the actual blast furnace gas composition like CO₂ 18-20% and N₂ 60% is expected to be similar to the result in this section.

In CO/CO₂ = 0/100, the gas composition is not actual. However, we investigate the behavior and phenomena as the model case in pure CO₂ condition due to gasification agent.

4.4. Spatial distribution of porosity

Cross-sectional digital images were taken by optical microscope (LV-100-POL, Nikon). Spatial distribution of porosity after gasification reaction was measured by image analysis (Winroof 5.01, Mitani Corporation). Conceptual diagram of the taking procedure of digital image is shown in Fig. 15. Coke samples were buried into resin, cut and polished. From end to end of coke samples, digital images were three times taken in each sample. Taking area of digital images (3.14 mm x 2.35 mm, 2.45 μm/pixel) was slid aside in half length of image size.

![Figure 15. A conceptual diagram of the taking procedure of digital image (Yamazaki et al., 2011)](image-url)
4.5. Reaction mechanism estimation of coke lump

In case of CO\textsubscript{2}/CO = 100/0, unreacted-core model was used to estimate the gasification reaction mechanism of coke lump. Using time change of conversion \( x_B \), dominant reaction mechanism of coke lump gasification can be estimated. Relationships between dimensionless reaction time \( t/t^* \) and conversion \( x_B \) when reaction controlling process is diffusion in boundary film, diffusion in product layer or reaction on the lump surface are expressed in Eqs. (7)-(9), respectively.

**Diffusion in boundary film:**

\[
\frac{t}{t^*} = x_B \equiv f(x_B) .
\]  \hspace{1cm} (7)

**Diffusion in product layer:**

\[
\frac{t}{t^*} = 1 - 3(1 - x_B)^{2/3} + 2(1 - x_B) \equiv f(x_B) .
\]  \hspace{1cm} (8)

**Reaction on or in the lump surface:**

\[
\frac{t}{t^*} = 1 - (1 - x_B)^{1/3} \equiv f(x_B) .
\]  \hspace{1cm} (9)

Relationship between \( t/t^* \) and \( f(x_B) \) of the dominant mechanism shows linear plot.

In case of CO\textsubscript{2}/CO = 50/50, homogeneous reaction model was used. Time change of weight loss can be represented by this model when chemical reaction progress uniformly in whole lump. Mass balance is expressed as equation connected with chemical reaction rate and time derivative of mass. If reaction gas concentration is constant while reaction of lump progresses, chemical reaction rate is proportional to ratio of residual solid. Mass balance is written as

\[
dx_B / dt = k(1 - x_B) .
\]  \hspace{1cm} (10)

Integrated with initial conditions \( t = t_0 \) and \( x_B = x_{B0} \), this can be written as

\[
x_B = 1 - (1 - x_{B0})\exp\{-k(t-t_0)\} .
\]  \hspace{1cm} (11)

If initial conditions \( t_0 \) and \( x_{B0} \) are equal to zero, the curve of Eq. (11) is through the origin. Weight loss curve is equal to Eq. (11) when lump reaction is controlled by chemical reaction.

4.6. Elastic modulus of coke-matrix

Elastic modulus of coke-matrix was measured by nano-indentation method. Load cycle indentation using sub-micron (or nano) indentation instruments is now a means of determining the deformation properties such as hardness and elastic modulus. A diamond tipped indenter with a precise geometry is pressed into a specimen with an increasing load up to a predetermined limit, and is then removed. The deformation properties can be determined using the load and displacement data obtained during the loading-unloading
sequence. In this study, calculating method of elastic modulus was based on the method proposed by Oliver et al. When Berkovich triangular indenter which has 115-degree in angle is used, elastic modulus $E_{\text{eff}}$ can be calculated by following formula:

$$h_s = 0.75 \frac{P_{\text{max}}}{S} \quad (12)$$

$$h_c = h_{\text{max}} - h_s \quad (13)$$

$$A = 23.97 h_c^2 \quad (14)$$

$$S = \frac{dP}{dh} = \frac{2}{\sqrt{\pi}} E_{\text{eff}} \sqrt{A} \quad (15)$$

$$\frac{1}{E_{\text{eff}}} = \frac{1 - \nu^2}{E} + \frac{1 - \nu_i^2}{E_i} \quad (16)$$

Resin-mounted specimens which are the same as ones mentioned in 4.2.4 were used again. Measurement parts of test specimen were outer region (vicinity of surface) and inner region (vicinity of center). Measurement conditions are shown in Table 4. The number of measuring points was 50 by each sample and gas composition.

| Indenter                        | Berkovich triangular pyramid |
|--------------------------------|------------------------------|
| Loading/unloading velocity     | [mN/s]                       |
| Maximum load                   | [mN]                         |
| Holding time in maximum load   | [s]                          |
| The number of measurements     | 50                           |

**Table 4.** Measurement condition of nano-indentation method

### 4.7. Results and discussion

#### 4.7.1. CO$_2$/CO = 100/0

Spatial distribution of porosity after the gasification reaction

Figure 16 shows spatial distributions of porosity before and after gasification. Plots are denoted as average value. In formed coke, porosity was distributed uniformly along the radial direction. In ferrous coke, in outer region, porosity was significantly large. Relationships between porosity of each part and conversion based on carbon mass of ferrous coke lump are shown in Fig. 17. Plots and error bars are denoted as average value and standard deviation, respectively. In outer region, porosity increased with an increase in progress of gasification. On the other hand, in inner region, porosity hardly changed. Figures 16 (b) and 17(a) show that there is “unreacted-core” in local porosity distribution in
ferrous coke after gasification reaction (CO\textsubscript{2}/CO = 100/0). It is suggested that chemical reactivity of gasification is advanced by the presence of iron-particles, and gasification in outer the coke lump is selectively progressed.

![Graph showing spatial distributions of porosity before and after gasification (CO\textsubscript{2}/CO = 100/0) of (a) formed coke and (b) ferrous coke (Yamazaki et al., 2010)](image)

**Figure 16.** Spatial distributions of porosity before and after gasification (CO\textsubscript{2}/CO = 100/0) of (a) formed coke and (b) ferrous coke (Yamazaki et al., 2010)

![Graph showing relationships between porosity of (a) outer region and (b) inner region and conversion based on carbon mass of coke lump in ferrous coke lump at CO\textsubscript{2}/CO = 100/0 (Yamazaki et al., 2011)](image)

**Figure 17.** Relationships between porosity of (a) outer region and (b) inner region and conversion based on carbon mass of coke lump in ferrous coke lump at CO\textsubscript{2}/CO = 100/0 (Yamazaki et al., 2011)

Cross-sectional images of formed coke and ferrous coke at 0.1, 0.2, 0.3, 0.4 and 0.5 in dimensionless radius before and after reaction under CO\textsubscript{2}/CO = 100/0 gas atmosphere is shown in Fig. 18. In *formed coke after gasification* ((b) in Fig. 18), coke-matrix between the two pores (pore-
wall) is thinning compared with before gasification reaction ((a) in Fig. 18). Microstructure at any dimensionless radius has the similar trend. An increase in local porosity shown in Fig. 16 should be due to the pore-wall thinning. There results show that whole coke lump uniformly embrittles. It is a matter of odds at where fracture origin is generated. Lump size may dramatically decrease due to lump fracture as split in fragments depends on the part of fracture origin. From the viewpoint of securing gas and liquid permeability in blast furnace, the increasing local porosity should be, therefore, avoided. In ferrous coke after gasification ((d) in Fig. 18), pore-wall in the region of 0.5 in dimensionless radius is dramatically thinning. Additionally, although most coke-matrix is continuing in other region, coke-matrix continuity is broken down in the region of 0.5 in dimensionless radius. These results indicate that the embrittlement occurs in the outer region of coke lump selectively; hence strength of whole coke lump can be maintained.

![Cross-sectional images of (a, b) formed coke and (c, d) ferrous coke at 0.1, 0.2, 0.3, 0.4 and 0.5 in dimensionless radius, respectively, before and after reaction under CO₂/CO = 100/0 gas atmosphere; Taking area of each picture is 3.14 mm x 2.35 mm.](image)

Figure 18. Cross-sectional images of (a, b) formed coke and (c, d) ferrous coke at 0.1, 0.2, 0.3, 0.4 and 0.5 in dimensionless radius, respectively, before and after reaction under CO₂/CO = 100/0 gas atmosphere; Taking area of each picture is 3.14 mm x 2.35 mm.

Reaction-controlling process of ferrous coke lump and formed coke lump are estimated. Figure 19 shows relationship between reaction time and conversion. In formed coke, weight loss behavior is not homogeneous reaction behavior despite uniform porosity distribution. In ferrous coke, at start of gasification, lump weight apparently increased due to oxidation of iron-particles by CO₂. Then lump weight decreased. Gasification reaction was terminated
at 0.2 minus minimum value of conversion. Reaction time from minimum conversion to termination conversion was similar to reaction time of formed coke. Figure 20 shows results of the reaction controlling process estimation for formed and ferrous coke. Equations (7)-(9) are plotted, respectively. The lines in Fig. 20 are regression line using least squares method. The largest $R^2$ (correlation coefficient) is focused since the dominant mechanism shows linear plot. Both dominant mechanism of ferrous coke and formed coke are diffusion in boundary film-controlling. Despite not the same spatial distribution of porosity (Fig. 16 (a) and (b)), each reaction controlling process is the same.

Reaction gas diffuses into inner region of coke lump after passing through the boundary film around coke lump. The fact shown in Fig. 16 suggests that there are different behaviors in the inner region after the reaction gas diffusion through boundary film although the each dominant mechanism is the same. Figures 16 and 17 suggest that the rate-controlling process of whole lump reaction is “diffusion in boundary film around the lump” in both formed and ferrous coke in pure CO$_2$ condition. In the whole gasification process, resistance of “diffusion in boundary film” overcomes resistance of other process; hence the rate of other process can be assumed infinite. In local process after diffusion into the coke lump, on the other hand, the both processes of formed and ferrous coke (i.e. chemical reactivity and its topology) should be compared as the process which has finite rate to tell the difference of not the same spatial distribution of porosity. In ferrous coke, the chemical reactivity is catalyzed by metal iron catalyst. It is supposed that reaction gas gasifies coke-matrix and consumes rapidly soon after diffusing into the lump due to iron catalysis. Hence, gasification in outer region of lump progresses selectively. On the other hand, in formed coke, chemical reactivity is not catalyzed; hence chemical reaction rate (not whole weight loss rate since reaction–controlling process is gas diffusion through the boundary film) should be slower than ferrous coke. In other words, formed coke shows the chemical reaction on or in coke-matrix slower than diffusion in the lump. The gas is, in addition, easier to diffuse into inner coke lump due to 50 vol. % in porosity. As a result, there is no the “unreacted-core” in spatial distribution of porosity.

![Graph](image.png)

**Figure 19.** Relationships between reaction time and conversion of (a)formed coke and (b) ferrous coke lump in CO$_2$/CO = 100/0 (Yamazaki et al., 2010)
Elastic modulus of coke-matrix

Elastic moduli of formed and ferrous coke-matrix before and after gasification are shown in Fig. 21 (a) Outer region, formed coke, (b) Inner region, formed coke, (c) Outer region, ferrous coke and (d) Inner region, ferrous coke).

In inner region, both cokes, elastic moduli were not significantly changed. In formed coke, despite spatial distribution of porosity after gasification reaction was uniform, elastic moduli between before and after reaction is not significantly different. Coke-matrix vanishing occurred at surface between coke-matrix and mm-order pore. Meanwhile, for a decrease in elastic modulus, gas must diffuse into nm-order pore. Therefore, it seems that there is the difference between gasification rate of the vanishing and a decrease in elastic modulus. In ferrous coke, the inner region is unreacted-core.

In outer region, significant difference of elastic moduli is shown between formed and ferrous coke. In formed coke, elastic modulus of coke-matrix significantly decreased. It is suggested that the gas sufficiently diffuses into nm-order pore in outer region, and nm-order pore increased. However, in ferrous coke, the elastic modulus did not decrease with gasification reaction. In outer region, also, it is suggested that coke-matrix vanishing is more rapid than the gas diffusion into the nm-scale pores. In other words, it is suggested that weight loss of whole ferrous coke lump is caused not by an increase in nm-order pore but by the coke-matrix vanishing. Microstructures of ferrous coke before and after gasification in outer region are shown in Fig. 22. Before gasification, iron-particles were completely surrounded by coke-matrix. After gasification, coke matrix surrounding iron-particles did not exist. Iron particle contacts with coke-matrix. Therefore, only coke-matrix vanishing may be promoted.
4.7.2. $\text{CO}_2/\text{CO} = 50/50$

**Spatial distribution of porosity after the gasification reaction**

Figure 23 shows spatial distributions of porosity before and after gasification. In both ferrous coke and formed coke, porosity was distributed uniformly along the radial direction. In ferrous coke, also, there was no unreacted-core. Figure 24 shows relationships between reaction time and conversion and results of the reaction controlling process estimation using Eq. (8). In ferrous coke, lump weight apparently increased due to oxidation of iron-particles.
by CO$_2$ the same as Fig. 19 (b). In order to estimate only the controlling process of gasification reaction, the results after weight increase are plotted. Both ferrous coke and formed coke, weight loss behavior of gasification was similar. In addition, the conversion curves are very closely followed by the estimation results. Lump reaction mechanisms are described by homogeneous reaction model. Solution-loss reaction is inhibited when CO is contained with reaction gas since CO absorbs competitively with CO$_2$ to active site on coke-matrix. Thus, the chemical reactivity in CO$_2$/CO = 50/50 is smaller than that in CO$_2$/CO = 100/0. So there is no unreacted-core since reaction gas CO$_2$ can diffuse enough into inner region of lump.

Figure 22. Microstructure of ferrous coke (a) before and (b) after gasification in outer region of coke lump in CO$_2$/CO = 100/0 (Yamazaki et al., 2010)

Cross-sectional images of formed coke and ferrous coke at 0.1, 0.2, 0.3, 0.4 and 0.5 in dimensionless radius before and after reaction under CO$_2$/CO = 50/50 gas atmosphere is shown in Fig. 25. After gasification ((b) in Fig. 25), both cokes have thinner pore-wall than cokes before gasification ((a) in Fig. 25). In ferrous coke, coke-matrix around iron particle, however, vanishes selectively, and continuity of coke-matrix is broken down; hence the strength degradation of ferrous coke seems to be more significant than that of formed coke.

Elastic modulus of coke-matrix

Elastic moduli of formed and ferrous coke-matrix before and after gasification are shown in Fig. 21 ((a) Outer region, formed coke, (b) Inner region, formed coke, (c) Outer region, ferrous coke and (d) Inner region, ferrous coke). In both cokes, elastic modulus in outer region decreases with gasification reaction. It is suggested that nm-order pore increases with gasification. However, a decrease in elastic modulus of ferrous coke-matrix (3.8 GPa) is smaller than that of formed coke (6.6 GPa). It seems that nm-order pore increment in volume of ferrous coke is smaller than that of formed coke.

Microstructures of ferrous coke before and after gasification are shown in Fig. 26. After gasification, coke matrix surrounding iron-particles did also not exist. Iron particles promote
coke-matrix vanishing, but inhibit a decrease in elastic modulus. Coke-matrix is vanished selectively around iron particles. This phenomenon indicates that gasification reaction part in coke lump can be controlled by addition of iron particle.

**Figure 23.** Spatial distributions of porosity before and after gasification (CO₂/CO = 50/50) of (a) formed coke, (b) ferrous coke (Yamazaki et al., 2011)

**Figure 24.** Results of the reaction controlling process estimation and relationship between reaction time and conversion based on carbon mass, (a) formed coke, (b) ferrous coke (Yamazaki et al., 2011)
**Figure 25.** Cross-sectional images of (a, b) formed coke and (c, d) ferrous coke at 0.1, 0.2, 0.3, 0.4 and 0.5 in dimensionless radius, respectively, before and after reaction under CO₂/CO = 50/50 gas atmosphere; Taking area of each picture is 3.14 mm x 2.35 mm.

**Figure 26.** Microstructure of ferrous coke (a) before and (b) after gasification in outer region of the lump in CO₂/CO = 50/50 (Yamazaki et al., 2011)
4.7.3. Discussion about the difference between CO2/CO = 100/0 and 50/50 from the viewpoint of the reaction type of coke lump (reaction-controlling process) and coke-matrix state

Reaction-controlling mechanism of coke lump

The rate constant of graphite or metallurgical coke in the case of CO2/CO = 50/50 is 10 times smaller than that in the case of CO2/CO = 100/0 (Miyasaka & Kondo, 1968; Turkdogan & Vinters, 1970). The reaction-controlling mechanism of coke lump changes from diffusion in boundary film to reaction on or in the lump surface due to the difference of chemical reactivity between each case of reaction gas composition.

In the case of CO2/CO = 100/0, both of formed coke and ferrous coke show similar weight loss curve due to the same reaction-controlling mechanism. The same rate of whole weight loss is, hence, shown by the both cokes (Fig. 19). However, in the case of CO2/CO = 50/50, both formed coke and ferrous coke show much different rate of weight loss each other due to chemical reaction-limited process of coke lump gasification. Ferrous coke shows the gasification rate about five times larger than the rate of formed coke. In comparison between the case of CO2/CO = 50/50 and 100/0, ferrous coke and formed coke show the rate difference of weight loss about three and seven times, respectively. Weight loss rate can be assumed to be similarly equal to chemical reaction rate in this condition. Thus, the difference of weight loss rate should be considered as the difference of chemical reactivity. Due to these differences, there are the changes of the state of coke-matrix in coke lump after gasification reaction.

Coke-matrix vanishing

Formed coke:

As shown in Figs. 16(a) and 23(a), local porosity uniformly increases due to gasification reaction in both gas compositions CO2/CO = 50/50 and 100/0. The porosity changes from about 50% to about 60 - 65% and each change shows a similar increase. Although there is the difference of elastic modulus between both gas compositions as shown in Fig. 21(a), the uniform change value of local porosity corresponds to 20% in the amount of weight loss based on the carbon weight before gasification reaction. To summarize above facts, both gas compositions CO2/CO = 50/50 and 100/0 have some gasification behaviors of coke lump in common as follows: (1) After gas diffusion into coke lump, reaction gas diffuses over a range of whole lump through the mm-order (macroscopic) pore, (2) In outer region of coke lump, a decrease in the elastic modulus is observed due to an increase in nm-order pore in coke-matrix; however, amount of a decrease in the elastic modulus slightly affects amount of coke-matrix vanishing, (3) In TRZ temperature during using highly reactive coke, not-catalyzed coke shows uniform spatial distribution of local porosity regardless of reaction gas composition.

Ferrous coke:

In gas composition CO2/CO = 100/0, coke-matrix in outer region of coke-lump is significantly vanished as shown in Figs. 16(b) and 17. Coke-matrix around the iron particle is more
vanished than the matrix not around the iron particle. In inner region, on the other hand, there is scarcely any change of coke-matrix. In addition, there is scarcely any change of the elastic modulus as shown in Fig. 21; hence coke gasification reaction in inner region hardly occurred. Reaction gas gasifies coke-matrix around the iron particle soon after diffusion into coke-lump from the outside and consumes. Hence, as a result, reaction gas hardly diffuses into inner region.

In gas composition $CO_2/CO = 50/50$, the behavior of coke-matrix vanishing is different from the case of $CO_2/CO = 100/0$. The vanishing occurs uniformly in whole ferrous coke lump as shown in Fig. 23(b). Although the iron particle vanishes coke-matrix surrounding it as the same for the condition of $CO_2/CO = 100/0$, spatial distribution of local porosity is uniform over a range of whole lump after gasification reaction. The uniform change value of local porosity of formed coke is the same as that of formed coke.

Formation of unreacted-core in local porosity:

Due to addition of iron catalyst, the unreacted-core is formed in the condition $(1173K, CO_2/CO = 100/0)$ in which formed coke forms no unreacted-core. On the other hand, in the condition $(1173K, CO_2/CO = 50/50)$, there is no unreacted-core after reaction. However, the behavior is observed that the coke-matrix around the iron particle is preferentially vanished. This fact suggests that it is possible to form arbitrary spatial distribution of local porosity by location of iron particle in coke lump due to the effect of preferential vanishing of coke-matrix.

Elastic modulus of coke-matrix

Inner region:

Both gas compositions $CO_2/CO = 50/50$ and $100/0$ show no difference of elastic modulus before and after gasification reaction whether or not formed coke or ferrous coke is gasified. Reaction gas diffusion seems to be difficult to occur into the bulk of coke-matrix because coke-matrix vanishing at surface of the matrix and mm-order pore is easier to occur than the diffusion into the bulk.

Outer region:

A decrease in elastic modulus occurs only in the outer region in both formed coke and ferrous coke. Each coke shows the different behavior of the decrease.

In formed coke, a decrease in elastic modulus significantly ($p < 0.05$) occurs before and after gasification reaction in both gas compositions $CO_2/CO = 50/50$ and $100/0$. Outer region of coke lump seems the part where reaction gas concentration is higher and reaction gas-exposed duration is also longer than inner region of the lump; hence reaction gas diffuses into bulk of coke-matrix, and nm-order pore volume increases.

In ferrous coke, no significant decrease in elastic modulus is observed in the case of $CO_2/CO = 100/0$. Coke-matrix around the iron particle is vanished in outer region, and the conversion of whole lump weight loss reaches 20mass% before occurring of coke-matrix embrittlement. On the other hand, in the case of $CO_2/CO = 50/50$, elastic modulus significantly ($p < 0.10$)
decreases. As discussed previously, in comparison between the case of CO₂/CO = 50/50 and 100/0, ferrous coke shows the rate difference of weight loss about three times. The longer time causes reaction gas diffusion into bulk of coke-matrix, and nm-order pore volume increases.

4.7.4. Concluding remarks and proposal

The results in section 4 are concluded as follows:

- Gasification of metallurgical coke lump was principally observed as microscopic vanishing of coke-matrix in mm scale.
- A decrease in elastic modulus involved with an increase in volume of nm-order pore in bulk of coke-matrix was hardly observed.
- Iron particle in coke lump plays the role of the catalyst of not so much the degradation but the vanishing of coke-matrix.
- Regardless of the reaction-controlling process difference of coke lump gasification, the chemical reactivity of coke-matrix which includes the effect of iron catalyst affects the spatial distribution of local porosity after gasification reaction. Therefore, controlling of iron particle alignment permits to control spatial distribution of local porosity and to form unreacted-core.

The study in this section shows relationship between gasification condition (temperature, gas composition and so on) and the formed spatial distribution of local porosity that affects the coke strength after gasification reaction. Particularly, the distinctive characteristic of coke-lump gasification which differs from gasification of other carbon material (i.e. electrode graphite and charcoal) is observed. Generally, a phenomenon of carbon material gasification in fine granule is observed as opened microscopic- or mesoscopic-pore increasing in carbon material, but a phenomenon of gasification of metallurgical coke lump is mostly observed as coke-matrix vanishing. Although coke-matrix degradation observed as a decrease in elastic modulus is also shown, the effect of the degradation on the relationship between coke-matrix vanishing and weight loss of whole lump is limited.

In previous study, it is noted that mm-pore structure in coke-lump affects the rate of weight loss of whole lump or pore structure after gasification in TRZ condition (temperature and reaction gas composition). In other words, gasification rate of whole lump is affected by reaction gas diffusion into inner region of lump rather than the gas diffusion into bulk of coke-matrix. Reaction gas diffuses into inner region of lump through the mm-pore of coke lump, and the gasification reaction mainly progresses on the surface between mm-pore and coke-matrix. The above mean that coke-matrix vanishing preferentially occurs than an increase in nm-pore volume and a decrease in elastic modulus and correspond to the results in this section.

In ferrous coke, the iron particle promotes vanishing of coke-matrix surrounding it rather than a decrease in elastic modulus. As discussed previously, degradation of coke-matrix is only limited, and the part where local porosity does not change seems to be never damaged. These facts suggest that spatial distribution of local porosity (in other words, formation of unreacted-core) can be controlled by alignment of iron particle.
The pre-addition method which is used in this section disperses catalyst iron particle in whole coke lump. Hence, coke-matrix in inner region of coke-lump is catalyzed as well as that in outer region. On the other hand, the post-addition method can disperse the catalyst particle locally. In addition, if catalyst particle is supported only in outer region of the lump, catalyst particle can remain in coke lump after gasification reaction (Yamamoto et al, 2010). To form unreacted-core that is not damaged, catalyst addition to only outer region seems to be useful. For the future, the method to control the spatial distribution of local pore or to form unreacted-core should be investigated as well as pre-addition method.

5. Conclusion

To realize the blast furnace operation in high carbon use efficiency, making of the coke which is satisfying high solution-loss reactivity and high strength is required. In order to make the coke which satisfies both the high solution-loss reactivity and the high strength, spatial distribution of local porosity of coke lump should be controlled as well as gasification reactivity of whole lump. In section 2, at first, the background of this issue was discussed. In section 3, the method to enhance coke solution-loss reactivity was briefly discussed. In section 4, the fundamental investigation and the proposal to support the reactivity and the strength at the same time was carried out. The essences discussed in these sections are summarized as follows:

Section 2:
- There are two iron reducing reactions (direct and indirect reaction).
- The direct reaction consumes solid carbon which is mainly metallurgical coke and is endothermic. In addition, the direct one occurs in the bottom part of blast furnace and affects the thermal balance in blast furnace and gas and liquid permeability, respectively; hence the ratio of direct reaction compared with that of indirect one should be decreased.
- The indirect reaction can be enhanced by change of C-O-Fe equilibrium state. The useful method for the change of equilibrium state is a decrease in TRZ temperature. The decrease can be achieved using highly-reactive coke.

Section 3:
- There are many elements which have catalyst activity of carbon gasification reacted by carbon dioxide (solution-loss reaction).
- Although there are the many kinds of catalyst that have good activity, calcium and iron are better element due to cost performance. Particularly, if Fe addition is used, iron ore as iron/steel making material is useful as the source of catalyst. In addition, iron ore in briquetted material before carbonization (mixed-coal/ore = 70/30) is almost reduced during carbonization (reducing ratio is ca. 95%). Hence, iron ore is available to use as catalyst source of highly-reactive coke. Therefore, iron seems the best material for highly-reactive coke in iron making process.
- There are two catalyst addition methods (post- and pre-addition).
Section 4:

- To maintain the strength after gasification, controlling of spatial distribution of coke lump is required.
- Gasification of metallurgical coke lump was principally observed as microscopic vanishing of coke-matrix in mm scale.
- A decrease in elastic modulus involved with an increase in volume of nm-order pore in bulk of coke-matrix was hardly observed.
- Iron particle in coke lump plays the role of the catalyst of not so much the degradation but the vanishing of coke-matrix.
- Regardless of the reaction-controlling process difference of coke lump gasification, the chemical reactivity of coke-matrix which includes the effect of iron catalyst affects the spatial distribution of local porosity after gasification reaction. Therefore, controlling of iron particle alignment permits to control spatial distribution of local porosity and to form unreacted-core.

To obtain useful knowledge, all we only need to know is the relationship between the quality of practical use and the history during falling to the bottom part of blast furnace or the coke making condition (procedure and material). However, to propose design and making guideline of metallurgical coke considering condition surrounding coke, investing the phenomena of gasification of whole coke lump is very important. For understanding the phenomena, both of macroscopic (reaction type of coke lump or coke-matrix state discussed in section 4) and microscopic understanding and relationship between both are needed (cf. Fig. 8).

Microscopic investigations for metallurgical coke gasification have been performed based on chemical approach (e.g. reaction mechanism analysis (Turkdogan & Vinters, 1970), gaseous adsorption property (Turkdogan et al, 1970; Kashiwaya et al, 2003; Kawakami et al, 2004), crystal structure analysis (Kashiwaya & Ishii, 1990) and so on) since the middle in 20th century. These investigations are fundamental and test specimen finely crushed, but coke is used as lump. The knowledge from the investigations is very important but is indirectly linked to the quality of practical use (e.g. strength before and after gasification and whole lump reactivity). In this chapter, the macroscopic phenomena were discussed.

In the future, it is expected that the model which combines microscopic phenomena and transport phenomena in coke lump during gasification and derives macroscopic phenomena will be developed. This helps to understand the gasification phenomena inclusively. In addition, it will be able to propose the proper guideline of design and making aggressively.

Author details

Yoshiaki Yamazaki

Department of Chemical Engineering, Graduate School of Engineering, Tohoku University, Sendai, Japan
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6. References

Ariyama, T. (2009). *Ferrum* (bulletin of ISIJ), Vol. 14: p. 781
Ariyama, T., Murai, R., Ishii, J. & Sato, M. (2005). *ISIJ International*, Vol. 45: p.1371
Bannya, S. (2000). *Ferrous Process Metallurgy*, The Japan Institute of Metals, ISBN 4-88903-013-1, Sendai, Japan
Carzorla-Amoros, D., Linares-Solano, A. & Salinas-Martinez de Lecea, C. (1992). *Carbon*, Vol. 30: p. 995
Fujimoto, H. & Sato, M. (2010). *J. Jpn. Inst. Energ.*, Vol. 89: p. 21
Grigore, M., Sakurovs, R., French, D & Sahajwalla, V. (2006). *ISIJ International*, Vol. 46: p. 503
Hayashizaki, H., Ueoka, K., Kajiyama, M., Yamazaki, Y., Hiraki, K., Matsushita, Y., Aoki, H., Miurata, T., Fukuda, K. & Matsudaira, K. (2009). *Tetsu-to-Hagané*, Vol. 95: p. 593
Hayashizaki, H., Ueoka, K., Ogata, T., Yamazaki, Y., Matsushita, Y., Aoki, H., Miura, T., Fukuda, K. & Matsudaira, K. (2009). *Tetsu-to-Hagané*, Vol. 95: p.460
Jaran, B. P. & Rao, Y. K. (1978). *Carbon*, Vol. 16: p. 175
Kamijo, T., Iwakiri, H., Kiguchi, J., Yabata, T., Tanaka, H. & Kitamura, M., (1987). *Tetsu-to-Hagané*, Vol. 73: p.2012
Kamishita, M., Tsukashima, Y., Saga, M., Miyagawa, T. & Tanihara, H. (1980). *Nenryo Kyokaishi*, Vol. 59: p. 757
Kashiwaya, Y. & Ishii, K. (1991). *Tetsu-to-Hagané*, Vol. 76: p. 1254
Kashiwaya, Y., Nakaya, S. & Ishii, K. (1991). *Tetsu-to-Hagané*, Vol. 77: p. 759
Kawakami, M., Taga, H., Takenaka, T. & Yokoyama, S. (2004). *ISIJ International*, Vol. 44: p. 2018
Kitaguchi, H., Nomura, S. & Naito M. (2007). *Kagaku-Kogaku-Ronbunshu*, Vol. 33: p. 339
Lahaye, J. & Ehrburger, P. (1991). *Fundamental Issues in Control of Carbon Gasification Reactivity*, Kluwer Academic Publishers, ISBN-13:9780792310808, Norwell, USA
Miyasaka, N. & Kondo, S., (1968). *Tetsu-to-Hagané*, Vol. 54: p. 1427
Miura, K., Hashimoto, K. & Silveston, P. L. (1989). *Fuel*, Vol. 68: p. 1461
Naito, M., Okamoto, A., Yamaguchi, K, Yamaguchi, T. & Inoue, Y. (2001). *Tetsu-to-Hagané*, Vol. 87: p. 357
Nishi, T., Haraguchi, H. & Miura, Y. (1984). *Tetsu-to-Hagané*, Vol. 70: p. 43
Nishi, T., Haraguchi, H. & Okuhara, T. (1987). Tetsu-to-Hagané, Vol. 73: p. 1869
Nomura, S., Ayukawa, H., Kitaguchi, H., Tahara, T., Matsuzaki, S., Naito, M., Koizumi, S., Ogata, Y., Nakayama, T. & Abe, T. (2005). ISIJ International, Vol. 45: p. 316
Nomura, S., Higuchi, K., Kunitomo, K. & Naito, M. (2009). Tetsu-to-Hagané, Vol. 95: p. 813
Nomura, S., Kitaguchi, H., Yamaguchi, K. & Naito, M. (2007). ISIJ International, Vol. 47: p. 245
Nomura, S., Terashima, H., Sato, E. & Naito, M. (2007). ISIJ International, Vol. 47: p. 823
Nomura, S., Terashima, T., Sato, E. & Naito, M. (2006). Tetsu-to-Hagané, Vol. 92: p. 849
Nomura, S., Higuchi, K., Kunitomo, K. and Naito, M. (2009). Tetsu-to-Hagané, Vol. 95: p. 813
Ohtsuka, Y., Kuroda, Y., Tamai, Y. & Tomita, A. (1986). Fuel, Vol. 65: p. 1476
Rist, A. & Bonnivard, G. (1962). Rev. Metall., Cah. Inf. Tech., Vol. 59: p. 401
Rist, A. & Meyerson, N. (1967). J. Met, Vol. 19: p. 50
Sears, J. T. Muralidhara, H. S. & Wen, C. Y. (1980). Ind. Eng. Chem. Process Des. Dev., Vol. 19: p. 358
Takarada, T., Ichinose, S. & Kato, K (1992). Fuel, Vol. 71: p. 883
Tomita, A., Ohtsuka, Y. & Tamai, Y. (1983). Fuel, Vol. 62: p. 150
Tomita, A., Takarada, T. & Tamai, Y. (1983). Fuel, Vol. 62: p. 62
Turkdogan, E., Vinters, J., (1970). Carbon, Vol. 8: p. 39
Turkdogan, E., Olsson, R. & Vinters, J., (1970). Carbon, Vol. 8: p. 545
Walker, P. L. Jr. (1968). Chem. Phys. Carbon, Vol. 4: p. 287
Watakabe, S. & Takeda, K. (2001). Tetsu-to-Hagané, Vol. 87: p. 467
Yamada, T. & Homma, T. (1979). Nenryo Kyokaishi, Vol. 58: p. 11
Yamamoto, Y., Kashiwaya, Y., Miura, S., Nishimura, M., Kato, K., Nomura, S., Kubota, Y., Kunitomo, K. & Naito, M. (2010). Tetsu-to-Hagané, Vol. 96: p. 297
Yamamoto, Y., Kashiwaya, Y., Miura, S., Nishimura, M., Kato, K., Nomura, S., Kubota, Y., Kunitomo, K. & Naito, M. (2010). Tetsu-to-Hagané, Vol. 96: p. 288
Yamamoto, T., Sato, T., Fujimoto, H., Anyashiki, T., Fukada, K., Sato, M., Takeda, K. & Ariyama, T. (2011). Tetsu-to-Hagané, Vol. 97: p. 501
Yamazaki, Y., Hayashizaki, H., Ueoka, K., Hiraki, K., Matsushita, Y., Aoki, H. & Miura, T. (2010). Tetsu-to-Hagané, Vol. 96: p. 536
Yamazaki, Y., Hiraki, K., Kanai T., Zhang X., Shoji, M., Aoki H. & Miura T. An Experimental Study on the Effect of Metallic Iron Particles on Strength Factors of Coke after CO2 Gasification Reaction, The 27th Annual International Pittsburgh Coal Conference, 48-3, Istanbul, Turkey, October 11-14, 2010
Yamazaki, Y., Hiraki, K., Kanai T., Zhang X., Matsushita, Y., Shoji, M., Aoki, H. & Miura, T. (2011). J. Therm. Sci. Tech., Vol. 2: p. 278