Recent Studies on the Properties of Blast Furnace Coke and Their Future Prospect*

By Yoshiaki MIURA**

Synopsis

This paper gives a general description of studies on blast furnace coke properties, encompassing their fundamental characteristics, and recent trends and future direction are also mentioned. As coke is porous composite material, study of crystalline structure, micro- and macrostructures, and coke functions is necessary, and for that purpose the theories and techniques of material science have been increasingly utilized.

I. Introduction

After the oil crisis, the economy entered a steady growth period with emphasis on resource and energy saving and adoption of "clean processes". For this type of economy, technical innovations in the field of materials supply will be needed and focus gradually changed from the conventional mechanical-strength-centered to the function-centered materials. As blast furnace coke performs three functions, namely, the function of fuel, that of reducing agent and that of a material which keeps furnace burden permeability, and especially strength in the high temperature zone of blast furnace is required of it, study of blast furnace coke genuinely pertains to its functional properties.

This paper, therefore, summarizes recent studies in this field which are swiftly moving toward the functional properties of coke. For further details which this paper may be found lacking due to limited space, please refer directly to reference material.

II. Orientation for Study of Coke Properties

The studies of blast furnace coke properties were, in a sense, studies without clear targets, although they were urged by practical necessities. This was because a lot of uncertainties shrouded the inner condition of blast furnace. In recent years, however, with the dissections conducted on blast furnaces which clarified the inner conditions the "science" of blast furnace has finally started and begun to give the basis upon which targets can be set up for the study of coke properties. The study of coke properties is located in the interface between the study of coke manufacture and that of coke use in the blast furnace, and therefore only when the targets for coke properties which are in agreement with blast furnace functions are identified, the quality design for coke will become possible, enabling the reaction design to be performed and the process design to be started for coke manufacture. Thus, a logical system of thought is established. In other words, the determination of coke properties is basic to development of such series of thoughts.

Some years ago, when blast furnace conditions became deteriorated, coke quality was immediately blamed. Currently, however, because the metallurgical coal situation has improved, and due to the efforts of researchers high quality coke is now made available, such baseless charge has ceased. Recent abrupt changes in the politico-economic situation have greatly altered the metallurgical coal situation and blast furnace operating conditions, urging us to establish a philosophy of coke manufacture based on the determined coke properties in line with the advancement of blast furnace theory.

III. Coke Structure and Properties—Viewed from a Standpoint of a Composite Material

The properties of chemical substances are determined by their structure. Coke structure can be studied in three stages: first, crystalline structure in the atomic and molecular dimensions, second, microstructure in the microscopic dimension (corresponding to coke matrix structure), and third, macrostructure in its industrial usage (coke lump structure).

The crystalline structure of artificial graphite has been clarified to a great extent by the progress of the science of carbon materials. In the case of the crystalline structure of blast furnace coke, which is governed by coking coal properties and carbonizing condition, the findings on artificial graphite cannot be directly applied to it because of significant differences in carbonizing process due to material characteristics and large effect of coexisting elements. The crystalline structure of coke carbon which is still to be clarified in many aspects, is being studied microscopically in its form of optical anisotropic texture because it affects the chemical reactivity and physical properties of coke.

The microstructure of coke concerns pore, pore wall, microfissure, etc., and directly affects the structural strength of coke matrix and diffusion condition in chemical reaction. These are governed by coking coal properties and homogeneity.

The macrostructure of coke concerns pore size and strength of lump coke. As quantitative assessment of coke macrostructure is difficult, it is tested by industrial testing method which is empirical and assessed in the form of quality index.

Thus, because coke structure is closely related to coke properties (functions), it is now necessary to study...
the relations between the coke functions and its structures such as crystalline structure, microstructure and macrostructure considering coke as a porous composite material, in order to clarify coke functional properties such as coke strength in the high temperature zone of blast furnace stated earlier. For this purpose the theories and techniques of material science should be applied to a large extent.

In coke manufacture, different kinds of coal are normally blended and carbonized in slot type ovens. In this case, different kinds of coal each having its own characteristic properties necessary for producing strong coke such as of low volatile matter, high carbon content, good fluidity when heated, high inert content which does not soften or agglutinate under heat, etc., are crushed to sizes optimum to each kind and mixed together. Namely a composite effect of these characteristic properties of different kinds of coal which compose a blend is aimed at.

A composite material can be defined as a material composed of two or more raw materials forming a phase different both physically and chemically and as a result having some useful function. For the study of such function, the following four viewpoints are necessary.3

1) Raw materials of composite material
2) Composite process
3) Composite structure
4) Composite effect

In coke manufacture, the raw materials of composite material are coking coal or petrographic components of coal, caking additives, etc., and the composite process corresponds to coal pretreatment and carbonization process. Also, the structure of product coke is a composite structure, and the composite effect covers various properties of coke. In view of coal blending as being fundamental to coke manufacture, the determination of coke properties as targets of coke manufacture can be considered as a matter of composite structure and composite effect seen from the viewpoint of composite material engineering.

The composite effect can be classified as shown in Table 1, where coke quality items related to each effect are listed in the right column. The relationships of these items, though subject to further study, are intended to show that this kind of approach is important and effective in coke quality study and for development of new coke manufacturing processes in the future.

From the standpoints of composite structure and composite effect, discussion will be made on evolution of stress, formation of coke lumps, and their properties in the carbonizing process as related to coke macrostructure. Then, the microstructure of coke including optical anisotropic texture will be discussed in relation to the mechanical properties of coke matrix. Further, the high temperature properties of coke which have been highlighted recently and lastly a few matters of coke manufacture required to obtain the coke structure and properties stated so far will be touched on.

IV. Formation and Strength of Coke Lumps

1. Fissure Generation during Coking Process

In the coal coking process, coal first softens, agglutinates, generates fissures in resolidified semi-coke due to contraction by volatilization, and produces coke lumps. Especially, the generation of fissures by contraction after resolidification forms together with the softening and agglutinating process one of the basic conditions for making coke from coking coal, and is an important factor governing the macrostructure (particle size) of coke in its industrial usage. However, while a number of studies have been made on the softening and agglutinating process from the viewpoints of the caking property of coal and coal blending, only few have so far been made on the resolidification-contraction process. This is partly because study of coke properties has been guided dominantly by empirical approach, as was pointed out earlier, with no clear idea on what is fundamental to the study of coke properties.

Studies on fissure generation by resolidification,

<table>
<thead>
<tr>
<th>Composite effect</th>
<th>Examples of items relating to coke quality</th>
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<tbody>
<tr>
<td>Raw materials effect</td>
<td>Additive effect</td>
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<tr>
<td>Effect that is able to prescribe only with the property and composition of raw materials</td>
<td>Complementary effect</td>
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<tr>
<td>Structural effect</td>
<td>Effect due to continuity-discontinuity of phase</td>
</tr>
<tr>
<td>Effect that is not able to prescribe only with the property and composition of raw materials</td>
<td>Shape and orientation effects</td>
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<td>Dimensional effect</td>
<td>Dimensional effect</td>
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<tr>
<td>Composite materials effect</td>
<td>Interface effect</td>
</tr>
<tr>
<td>Effect that is revealed only with compositeness</td>
<td>Different phase effect</td>
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treating quantitatively from the dynamic aspect were made by CERCHAR (Centre d'Etudes et Recherches des Charbonnages de France),4-6) by Yoshida in Japan7,8) at about the same time, later by BCRA in the U.K.,9~ by Filonenko et al.,10-12) and by VUKhIN* in the U.S.S.R.13~20~ Major points of these study reports will be taken up mainly from those of CERCHAR and Yoshida.

According to Yoshida, the degree of coke fissuration (primary fissure) is proportionate to the volatilizing rate per unit quantity of semicoke at the resolidification temperature of coal, \(-\frac{dm}{dt}(1/m)\), \((\equiv \text{pyrolysis coefficient}, F_1, \text{where} \(m\): \text{semicoke quantity}, t: \text{time})\), and the following relation is established.

\[
N = k\left(\frac{4e}{2A}\right)^{1/2}\left[-\frac{dm}{dt} (1/m)\right]^{3}
\]

where, \(N\): Number of fissures
\(k\): Proportional constant
\(\Delta\theta\): Time from the start of strain energy accumulation to the generation of primary fissure
\(A\): Area of primary fissure
\(\tau\): Surface tension

The \(F_1\) here can be considered equal to the contraction coefficient at resolidification temperature, \(1/L (dL/d\theta)\), in the study of CERCHAR,6 where \(L\): length of specimen, \(\theta\): temperature**. This contraction coefficient is greater with coal of higher volatile matter, as shown in Fig. 1, and hence entails greater degree of fissuration.

The mechanism of fissuration is considered as follows. Now, take a unit thin layer of coal (slack) and heat it from below, as shown in Fig. 2. It will be found that the side of lower temperature (top AB) has larger contraction coefficient near resolidification temperature than the side of higher temperature (bottom A'B'), as shown in Fig. 1, and the semicoke bends up as shown in Fig. 2. In the actual coke oven, internal stress develops in the coal layer by restraints from oven wall, weight of coal charge, swelling pressure of neighboring layer, etc., and grows, as shown in Fig. 3, with the rise of heating surface temperature. As tensile stress works on the surface of coke cake contacted to the oven wall, fissuration occurs when the magnitude of tensile stress exceeds the breaking strength of semicoke matrix.

2. Stress Distribution in Oven Chamber and Coke Size

As was discussed in the preceding section, coal particles soften and agglutinate to form a mass in the oven chamber. However, because temperature gradient exists in the oven chamber, thermal stress which develops above resolidification temperature (Fig. 3) produces primary fissure where the mass contacts the oven wall.*** As this fissure continues to grow, coke lumps are finally produced. The primary fissure is thus an important factor which governs lump coke size. Hence, it becomes necessary to find stress distribution in the oven chamber.

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** It is assumed here that the heating rate is constant and that the weight loss is proportional to the amount of contraction.

*** Microscopically, the difference in swelling or contraction rate existing between the fused part and the non-fused part of coal particles is partly responsible for fissuring.
Although studies on these phenomena were made mostly in the U.S.S.R., Japanese studies in this field can be expected with the systematization of coke quality study. Introduction of a few U.S.S.R. reports will be given in the following section.

First, Konyakhin et al.\textsuperscript{21) conducted modelling of coke cake surface layer as shown in Figs. 4 and 5, in order to analyze stress distribution in the coke cake surface layer in its initial stage of forming against the heating front in the carbonizing chamber. Namely, assuming tensile stress in $A$, compression stress in $B$ and bending moment, $M$, working in $B$, they presented an equation for calculating each of them. Nechaev and Gryaznov\textsuperscript{17)} indicated that the mean size, $d_m$, of product coke can be calculated using the equation below from the carbonizing period, $P$, final carbonization temperature, $T$, thermal diffusivity, $\alpha$, and coke properties (Young's modulus, $E$, contraction coefficient, $\varphi$, and tensile strength, $\sigma$).

$$d_m = 5 \sqrt{\alpha P E \varphi T}$$

3. Strength of Lump Coke

The strength of lump coke in its macrostructure is influenced by various factors (fissure, microstructure, factors related to manufacturing condition, etc.) and it is difficult to indicate it by any absolute value of physico-chemical dimension. Hence, in practice it is indicated by strength index obtained by various empirical test methods.

The strength property of coke is normally classified into crushing strength and abrasion strength. Here, the crushing strength\textsuperscript{*} means the resistance of coke to breakage into small pieces by dropping, compression or impact, and the abrasion strength is a property determined by coke matrix texture and structure.\textsuperscript{22)} As for the testing methods for these strength indices, no explanation will be given in this paper because they are indicated in the Japanese Industrial Standards\textsuperscript{23)} and a great number of technical reports.

In practice, a revolving drum tester is frequently used. Wallach and Sichel\textsuperscript{24)} analyzed the relation between the drum revolutions of the tester and the breaking behavior of lump coke statistically, and obtained indices corresponding to the crushing strength and the abrasion strength, discussed above, from the size distribution of broken product. Normally, when the number of revolutions is increased, the amount of fines generated indicates the resistance of coke to abrasion as more abrasion factors come to be involved. Nagata\textsuperscript{25)} studied the breaking mechanism of lump coke. Detailed study of breaking mechanism in relation to coke structure will, therefore, become necessary. For more information on coke strengths, refer to a recent paper of Nishi on general treatment of the subject.\textsuperscript{26)} Further, for the strengths of lump coke, its macrostructure in the oven chamber and quality problem of segregation are attracting the attention of the people concerned. These topics will be treated in Chapter VII in the paper.

\* The German term "Stückfestigkeit" is meant here. However, because no appropriate English word can be found, this term is used. The "crushing strength" used conventionally in Japan often meant the index obtained by revolving drum test (normally 30 revolutions), and hence for the indication of such index the term "drum strength index" adopted in JIS\textsuperscript{20) should, in author's opinion, be used.
V. Microstructure and Mechanical Properties of Coke

1. Microstructure of Coke

Coke, a porous composite material, is made up of pores and pore wall. These are produced by fusion or sintering of coal particles, and for them two microstructural models can be worked out as shown in Fig. 6. The aggregate type (A type) is the one in which coal particles fuse together by sintering leaving voids between particles as pores. On the other hand, the sponge type (S type) has bubbles generated after complete fusion of coal particles. In actual coke manufacture, however, an intermediate structure is often found. Fine pores are also produced not only between particles but within individual particles by gas from the thermal decomposition of coal substance. High-fluidity coal or coal charge with caking additive produces a structure close to the S type, while a coal charge containing a large quantity of non- or slightly caking coal produces a structure close to the A type.

Among pore characteristics, porosity, pore size, pore-size distribution, shape, etc., need to be taken into consideration. Except for the volume porosity obtained from the density measurement, only a few studies have been made on them. In comparatively recent years, a number of papers have been published on them, but because coke pores range from micropores of angstrom (Å) order to macropores of millimeter order, no method which is capable of measuring all of them is available. Also, little has been investigated concerning the effect of these pore sizes on coke quality.

Pores of angstrom order can be measured by the method which utilizes gas absorption, and pores ranging from 20 Å to 0.25 mm can also be measured by the mercury penetration method. Pores of millimeter order are measured by use of low-magnification optical microscope.

For measurement by optical microscope, the method adopted by Abramski and Mackowsky, though somewhat old, is well-known, and the following items are measured.

- **Dichtigkeit**: Ratio of pore wall area to pore area
- **Porigkeit**: Index for the smallness of pore
- **Zelligkeit**: Index for the thinness of pore wall
- **Porenmittel**: Mean pore diameter
- **Wandmittel**: Mean pore wall thickness

![Aggregate (A type) Sponge (S type)](image)

Fig. 6. Microstructural model of coke.

Because application of this method is done by manual measuring and thus requires a long time plus a complicated procedure, recently automatic measuring methods combining a television system with a computer have been devised. Among them, the automatic image analyzer by Patrick et al., is well-known. Measurable by this method are total porosity, perimeter of pore, number of pores, distribution of pore diameters, distribution of pore wall thicknesses, Feret diameter, shape factor of pore, etc. Clarification of physico-chemical characteristics as well as pore characteristics of coke by the use of these methods is expected.

The pore wall is made of carbon substance which makes up coke, and the chemical composition by elemental analysis and ash component analysis, optical anisotropic texture and degree of crystallization can be considered as structural factors of pore wall. Ramdohr is said to be the one who first reported on the optical anisotropy of coke carbon, but subsequently since Mackowsky pointed out relations between the mosaic structure component of this optical anisotropy and fluidity of coking coal, and Brooks and Taylor reported on the change of anisotropic texture during carbonization of pitch and similar substances, this subject has become a focus of interest. Sugimura et al. and Goldering published representative papers on this subject carrying their study results on textures from that of fine mosaic structure to that of flow structure and relationships with the degree of coalification of coking coal. In connection with this, measurement of reflectance and bireflectance of coal, semicoke and coke has been conducted as a quantitative method of tracing carbonizing process. For detailed information on this, refer to Murchison's report.

Finally, the degree of crystallization, i.e., degree of graphitization, which is another structural characteristic of pore wall, is investigated by X-ray diffraction method. This is done for relative comparison between specimens although the pore wall of coke does not show clear diffraction pattern like graphite because of differences in raw material and carbonizing conditions.

2. Microstructure and Mechanical Properties

Coke is regarded as a brittle material and known to generate brittle fracture under external force. Hence, Griffith's theory of brittle fracture can be applied to coke. Namely, the structural defects of coke such as microfissures in coke act as stress concentration points, reducing the strength of coke matrix. According to Griffith, the breaking strength can be expressed by the equation below.

\[ \sigma = \sqrt{2\gamma / \pi e} \]

where, \( \sigma \): Breaking strength, called Griffith stress,
As evident in Griffith’s equation, the greater the Young’s modulus of caking additives, and smaller size of coke breeze added. Isobe et al.,47) conducted a statistical simulation analysis of the elastic behavior of coke and the analysis of change in Young’s modulus by applying the composite rule. Their report can be marked as indicating a new future direction of study techniques.

For the relations between microstructures and mechanical properties of coke, as has been discussed above, study has just started positing coke as a porous composite material for a study subject of material science, and future progress in this study is greatly expected. From the practical point of view, it is clear that uniform microstructure with less structural defects is important for maintaining the mechanical properties of coke matrix, as can be exemplified by the result48) of study on material strength to which Weibull’s theory of statistics was applied. As a result, high-temperature properties of coke are now being studied in various respects from both the microscopic and macroscopic aspects. However, ideal high-temperature properties of coke have not yet been determined because it is difficult to accurately grasp the conditions to which coke is exposed in the high-temperature zone of blast furnace including the raceway, or to carry out experiment at high temperatures. This poses an important future subject of study.

In this chapter, therefore, a few matters which can be considered as fundamental to the study of the high temperature properties of coke will be discussed. Recent general expositions by Miyagawa,50) Okuyama51) and Tate52) deal with items related to this subject.

1. Behavior of Coke in Blast Furnace

The dissections of blast furnaces conducted by Nippon Steel Corp. ascertained that lump coke charged into the blast furnace remains almost intact down to the middle part of the shaft and starts to change its properties in the lower part of the shaft. The degree and involvements of this change are considered to differ according to the furnace size, operating conditions, and coke quality before charging.

In principle, however, it can be assumed that lump coke size degrades as it becomes porous and brittle by selective solution loss reaction of coke texture components and is subjected to abrasion during descent in the furnace and mechanical impact in the raceway. These phenomena were confirmed in the subsequent dissections54-57) and gave a strong impetus for promotion of study of coke high-temperature properties. On the other hand, during short shutdown periods samples are taken out of blast furnaces at the tuyere level using tuyere sampler, and valuable data are being collected on the change of coke properties.58-60) A systematic study of coke sampled through tuyeres is under way61,62) at ECSC in the U.K. The samples in this case are raked out through tuyeres during temporary shutdowns. Various problems arising from these field tests still require solutions. They can be summarized as follows.

1. Method of Sampling Charged Materials from Blast Furnace

The samples taken by dissection, regardless of the manner of quenching either by water or inert gas, are cold samples and therefore give only limited information on iron ore, molten slag, metal and coke. Even with the tuyere sampler, problems remain regarding the sampling point in the furnace or whether or not samples, especially in the case of coarse materials, are uniform without segregation. Hence, improvement of these methods and development of
new techniques have to be carried out.

2. Inner Condition of Blast Furnace

For assessing coke behavior in the blast furnace and the high-temperature properties of coke from the results of sample analysis for coke properties, it is necessary to obtain accurate comprehension of the inner conditions of blast furnace such as temperature, composition of atmosphere (gas, alkali, sulfur compounds, etc.), pressure and packing structure (cohesive zone, movement of dead-man coke, etc.), and their relations to blast furnace operating conditions. These data will become available with the advance of furnace condition measuring systems, simulation computations, and dissections. On the other hand, they have immense significance on the interpretation and assessment of the results from laboratory simulation experiments on high-temperature properties of coke. The study of coke quality without definite targets, discussed in Chapter II, can be attributed to this fact, and hence the coke quality study tended to be endless in the past.

3. Mechanism of Coke Deterioration in the High-temperature Zone of Blast Furnace

The basic pattern of coke deterioration has become clear through dissections and study of samples taken through tuyeres. On the other hand, however, much is now unknown concerning the mechanism of size degradation of coke and the mechanism of coke fine generation in the high-temperature zone which is the essential part of the blast furnace. For their clarification, however, much depends on further advances in the measuring systems discussed earlier.

4. Parameters for High-temperature Properties of Coke

A number of parameters for high-temperature properties of coke obtained by applying various test methods have been reported to date. Major ones can be reduced to the CO₂ reactivity and the high temperature strength of coke. Of them the high temperature strength has especially drawn attention for its practical value. Those reports which have been published on this subject can be listed up as given in Table 2. Among them the so-called "Hirohata Method" which is based on the coke strength after CO₂ reaction by small sample (abbreviated as CSR: Coke Strength after CO₂ Reaction) is most used. Because this method requires comparatively simple measuring and produces fairly good correlations with blast furnace operating indices, people have now started to use it not only in Japan but also in Europe.

However, as was discussed earlier, because the blast furnace conditions were not accurately understood, the signification of the CSR-index is not necessarily definite leaving some uncertainties. Presently, this index is used in a limited scope of process control (blast furnace operation and coke manufacture) and its utility should be interpreted as such. In the future with the further clarification of blast furnace conditions, development of more rational parameters for high-temperature properties of coke will be required.

2. Changes in the Properties of Coke by High Temperature Reaction

When coke is heated to high temperatures under blast furnace conditions, pores of coke change their state with the progress of graphitization of coke carbon and the volatilization of inorganic components.

<table>
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<tr>
<th>No.</th>
<th>Kind of test</th>
<th>Description</th>
<th>Reference</th>
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<tbody>
<tr>
<td>1</td>
<td>High temperature drum strength (drum with ball)</td>
<td>Measured by revolving drum with steel or porcelain ball at ( \sim 1000^\circ \mathrm{C} ) under ( N_2 ) atmosphere.</td>
<td>64~67</td>
</tr>
<tr>
<td>2</td>
<td>High temperature drum strength (drum without ball)</td>
<td>Ditto, without ball, max. 1 500 (^\circ)C.</td>
<td>68~70</td>
</tr>
<tr>
<td>3</td>
<td>High temperature crushing strength</td>
<td>Measured at ( \sim 1400^\circ \mathrm{C} ) under ( N_2 ) atmosphere.</td>
<td>80, 81</td>
</tr>
<tr>
<td>4</td>
<td>High temperature impact strength</td>
<td>Measured by dropping the coke under the hot ( N_2 ) atmosphere (( \sim 1000^\circ \mathrm{C} )) or impacting with hot air.</td>
<td>82, 83</td>
</tr>
<tr>
<td>5</td>
<td>Drum strength during CO₂ reaction</td>
<td>Measured at high temperature with CO₂ gas.</td>
<td>84, 85</td>
</tr>
<tr>
<td>6</td>
<td>Drum strength after CO₂ reaction</td>
<td>Measured at ambient temperature after CO₂ reaction at high temperature.</td>
<td>86, 87</td>
</tr>
<tr>
<td>7</td>
<td>High temperature drum strength after CO₂ reaction</td>
<td>Measured at high temperature under ( N_2 ) atmosphere, after CO₂ reaction at high temperature.</td>
<td>88</td>
</tr>
<tr>
<td>8</td>
<td>Disintegration property during CO₂ gasification</td>
<td>Measurement of disintegration of coke during CO₂ gasification in fluidized bed at high temperature with ( O_2 ) free CO₂ gas.</td>
<td>89, 90</td>
</tr>
<tr>
<td>9</td>
<td>High temperature tensile strength</td>
<td>Measured at high temperature.</td>
<td>91</td>
</tr>
<tr>
<td>10</td>
<td>Testing furnace simulated to combustion at the front of tuyere</td>
<td>Investigation of the combustion characteristics of coke and the behavior of race way, using packed bed of coke.</td>
<td>92, 93</td>
</tr>
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* The Research Subcommittee on the Method of Measuring High Temperature Properties of Coke was formed in the Coke Committee of ISIJ in April, 1980, to investigate the use of this method by Japanese steelmakers, and is now conducting experiments to check the results using common specimens.
On the other hand, coke carbon is gasified by CO₂ reaction, etc. As a result, coke matrix deteriorates and coke reduces its strength and size, followed by generation of fines. On such changes in the properties of coke at high temperatures, a large number of studies have so far been made both in Japan and abroad. Especially, in recent years, researches have been actively conducted on conditions for manufacturing coke of excellent high temperature strength. In this case, however, because the deterioration of coke is closely related to its own texture and structure, relevant research targets which suit the purpose must be established, but, as has been repeatedly pointed out, ideal coke texture or structure is not yet understood.

From the practical standpoint, the “strength after CO₂ reaction” is considered important. Study on this coke strength seems to be based on the following two assumptions.

1. The strength after CO₂ reaction is a coke property completely different from the conventional coke cold strength, and the factors governing it are also different.

2. Reaction temperature is also assumed to be over 1 500 °C toward the combustion zone near tuyeres in the blast furnace. Hence, the effect of the components which concentrate in the high-temperature zone of blast furnace such as alkali, sulfur and zinc must be taken into consideration. Papers presented to the symposium of the 99th ISIJ Meeting held in April, 1980, were mostly research papers along this line. General discussions will be given in the following section on the changes in the properties of coke at high temperatures in three areas: change in chemical structure, deterioration by thermal effect, and deterioration by CO₂ reaction.

### 1. Changes in Chemical Structure and Composition of Coke by High-temperature Reaction

Coke can be divided into the soft carbon coke which is relatively easily graphitized when heated at high temperature and the hard carbon coke which is hard to graphitize by heating at high temperature. If these are applied to metallurgical coals, the metallurgical coals are arranged in the order shown below.

Medium volatile bituminous coal > low volatile bituminous coal > High volatile bituminous coal

The medium volatile bituminous coal is shown to be the most susceptible to graphitization. Normally the degree of graphitization is indicated by \( L_a \) (size of crystallite in the direction of \( \alpha \)-axis) and \( L_c \) (size of crystallite in the direction of \( \epsilon \)-axis) obtained by X-ray diffraction as parameters. Soft carbon has remarkable growth of \( L_a \) above 1 000 °C, but the growth of \( L_a \) is gradual up to about 1 500 °C, becomes fast beyond 2 000 °C exceeding 100 Å, and reaches a few thousand Å around 3 000 °C. Although hard carbon is said to have progress of graphitization above 2 000 °C, graphitization progresses only locally.

When coke is heated to high temperature, desorption of absorbed gas occurs, and such components as ash, sulfur, nitrogen and phosphorous decrease. Although sulfur is studied in connection with coal and coke desulfurization, and nitrogen in connection with NOₓ measures for environmental protection, there still remain a number of uncertainties concerning their modes of existence.

### 2. Deterioration by Thermal Effect

The important point in the thermal deterioration of coke is that microfissures apparently close within a certain limit or develop into macrofissures as they increase due to differences in expansion or contraction between optical anisotropic textures of matrix part of coke structure. In this case, the mechanical properties of coke matrix are often indicated by parameters including hardness, Young’s modulus, and breaking strength (tensile strength and bending strength).

When checked from these viewpoints, the existing data show that the microhardness decreases above 1 000 °C due to the progress of graphitization, as mentioned before, that tensile strength rather increases up to about the carbonization temperature (~1 300 °C) as microfissures close by slight expansion of coke, and that tensile strength decreases beyond that temperature as microfissures increase because of contraction of coke. Further, porosity increases with the volatilization of ash content by the rise of temperature, constituting one of the factors responsible for strength decrease. In addition, drum strength also starts to decrease near 1 300 °C. The micro-strength which has been considered as indicative of the matrix strength continues to increase with the rise of heating temperature, posing a necessity to reinterpret this index.

### 3. Deterioration by CO₂ Reaction

Deterioration by CO₂ reaction includes the deterioration of mechanical properties, decrease of strength, degradation of particle size and generation of fines by selective gasification of texture components of coke pore wall caused by the reaction between coke matrix and gas consisting mainly of CO₂ (including the catalytic reactions of coexistent alkali, etc.). Among the reactions between coke and gas, the following three major reactions are studied.

\[
\begin{align*}
C + O_2 &= CO_2 \\
C + H_2O &= CO + H_2 \\
C + CO_2 &= 2CO
\end{align*}
\]

These reactions correspond to the solution loss reaction (Eqs. (2) and (3); Eq. (3) is more important as it is quantitatively greater than Eq. (2)) taking place both in front of tuyeres and in the shaft and to the combustion reaction (Eq. (1)) occurring in front of tuyeres. Also, from a chemical kinetic study of the mechanism of lump coke degradation by gasification reaction, the rate of coke fines generation, \( V \), can be obtained by the following equation.

\[
V \propto [(1 - f_a)/f_a] \cdot (K_eD_a)^{1/2}
\]
where, \( f_r \): Critical ratio of gasification
\( K_c \): Volumetric reaction rate constant of lump coke
\( D_e \): Effective diffusion coefficient of gas in coke particle

In this equation, both \( f_r \) and \( K_c \) can be regarded as the terms related to the properties of coke matrix, i.e., pore wall, and \( D_e \) as the term concerning pores of coke.

The discussion above has briefly described coke deterioration by CO\(_2\) reaction. Although a large number of reports are available on coke manufacturing conditions, coke texture and structure, ash components of coke such as alkali, blast furnace conditions, etc., as factors influencing reaction rate formulae and reactivity of coke, no discussion will be given on them due to limited space. Therefore, refer to reports such as listed in the references of this paper. For the strength after CO\(_2\) reaction which is important in practice, the previous chapter has to be referred back to.

The deterioration by CO\(_2\) reaction is a phenomenon interlaced with the deterioration by thermal effect, and hence separation of its factors from those of the latter is difficult. Also, because the phenomenon progresses by the selective gasification reaction of coke components, and the degree of homogeneity of texture component greatly affects the effect of deterioration (strength after CO\(_2\) reaction), the reproducibility of strength measurement is not always high. As a result of a great number of studies, phenomena and facts on particular subjects have been quite well accumulated, but these are not yet integrated into one picture as a system of thought, requiring further efforts. Especially, as will be pointed out in the following chapter, an ideal situation from the standpoint of coke manufacture will be that the estimation of the high temperature properties of coke become possible.

**VII. Making up Coke Quality**

The aim of study of coke manufacture is to establish the conditions for the stable manufacture of quality coke. This “quality” must be which is determined to suit the purpose of use in the blast furnace. In practice, this quality may be the quality parameter average of mass of lump coke used in the blast furnace, but from the standpoint of coke manufacture it should desirably be a quality index based on the coke texture and structure coming out of the coking coal carbonizing process. Once this is done, the quality parameter for effective operation control can be set up. Hence, in this chapter, discussion will be dedicated to one* of the ultimate aims of study on coke properties, i.e., “making up” coke quality which is the setting up of the conditions of a composite process for a porous composite material like coke.

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* Another factor may be the establishment of the conditions for use of coke through the clarification of the reaction behavior of coke in the blast furnace.  
* This indicates the process of the suppression of the plastic layer swelling by the resistance of a solidified adjacent semicoke layer, resulting in the anisotropy of pore shape.
carried out only from experience under limited conditions. Namely, for the effect of coal blending which conventionally had the largest bearing on coke quality an empirical rule is established through accumulation of information as data on coal blending theory and blending standards. For this information, refer to the author's general expositions. Also available is a method of coke quality estimation by Simonis which takes into account the manufacturing conditions (charge coal particle size and heating condition) besides coal properties.

For the future coke quality estimation, approach to the manufacturing conditions through the media of coke texture and structure especially in consideration of the high-temperature properties of coke will be necessary. In this case, factors involved in the manufacturing conditions can be largely divided into three categories: first category for coking coal properties, second for pretreating conditions, and third for carbonizing conditions. Accordingly, coke quality is determined as a function of these three types of manufacturing conditions. More realistically, it is important to obtain experimental knowledge of coking coal properties, to theorize factors related to pretreatment and carbonization, and to arrange the relations among the factors of these three items in the form of an empirical equation of correlations, relating them to the coke structure and quality. As an attempt of this nature, attention may well be paid to the recent report by Suginobe et al. They investigated into the substance of coke drum strength, and considering the tensile strength of semicoke as one of the forming factors, they theoretically obtained as governing tensile strength the C factor for caking of coal particles in the carbonizing process. Further, considering the fissures generated under thermal stress in semicoke as the second forming factor, they derived it as the F factor through theoretical process. Then, they established a method of estimating the drum strength (DI) by experimentally obtaining these two factors from proximate analysis of coking coal, Gieseler's fluidity, crushed coal particle size, and flue temperature during carbonization.

VIII. Conclusion

As regards the study of blast furnace coke quality, its fundamental character, recent trends and future directions have been discussed briefly. Conventionally, this field of technology has been predominantly led by empirical knowledge. The author presents as part of this paper his personal suggestions as to how a theoretical system of thought should be established for changing this research pattern in order to bring about further innovations in this field.

Because this subject of blast furnace coke quality encompasses a wide range of basic knowledge and a variety of technological fields, the author apologizes some improper expressions or irrelevancies may be found in this paper. However, the author wishes what he wants to say will be well understood.
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