

# Characterization of Thermal Annealing Effects on the Evolution of Coke Carbon Structure Using Raman Spectroscopy and X-ray Diffraction

Masahiro KAWAKAMI,<sup>1)</sup> Haruki KANBA,<sup>1)</sup> Kazunori SATO,<sup>1)</sup> Toshihide TAKENAKA,<sup>1)</sup> Sushil GUPTA,<sup>2)</sup> R. CHANDRATILLEKE<sup>2)</sup> and Veena SAHAJWALLA<sup>2)</sup>

1) Department of Production Systems Engineering, Toyohashi University of Technology, Tempakucho-aza-Hibarigaoka 1-1, Toyohashi 441-8580 Japan. E-mail: kawakami@seiren.tutse.tut.ac.jp 2) Cooperative Research Centre for Coal in Sustainable Development School of Materials Science and Engineering, The University of New South Wales, Sydney NSW 2052 Australia.

(Received on February 9, 2006; accepted on May 12, 2006)

An experimental study was conducted to monitor the evolution of coke carbon structure during thermal annealing in a temperature range from 1 273 to 2 473 K in a bench-scale reactor. Coke carbon structure was characterized by using Raman Spectroscopy and the X-ray Diffraction. The Raman spectra of most of the cokes displayed two broad peaks G\* (1 620 cm<sup>-1</sup>) and D\* (1 360 cm<sup>-1</sup>). Both Raman peaks were deconvoluted into five peaks namely G, D, D', R<sub>1</sub> and R<sub>2</sub>. On the basis of area under the respective band peaks, new structural parameters were obtained to quantify graphitic (G), graphitic defect (D) and random (R) carbon fractions of cokes.

XRD analysis was used to show that stack height carbon crystallite, L<sub>c</sub>, of coke increases with increasing annealing temperature while the impact of annealing duration was not significant particularly up to 1 873 K. On the other hand, average carbon crystallite width, L<sub>a</sub>, did not improve significantly up to 1 873 K, and increased rapidly after subsequent rise in the annealing temperature. It appears that during annealing up to 1 873 K, modification of coke carbon structure could occur due to loss of basal carbon as a consequence of *in-situ* gasification.

The lateral expansion of carbon crystallite, L<sub>a</sub>, was related to relative intensity or shape of Raman band peaks such that both parameters did not change significantly up to an annealing temperature of 1 873 K. At higher annealing temperatures, L<sub>a</sub> values of coke increased with decreasing D/G ratio. Lateral expansion of carbon crystallite was attributed to progressive reduction of defects of graphitic carbon of coke, which can be monitored by D fraction of Raman Analysis. Combined Raman and XRD analysis suggested that rapid graphitization of coke may not occur along all dimensions until the annealing temperature exceeds 1 873 K.

Combining XRD and Raman analysis would provide a comprehensive evaluation of the evolution of coke carbon structure at different temperatures and their subsequent implications on the efficiency of various ironmaking operations.

KEY WORDS: coke; Raman spectroscopy; XRD; annealing; structure evaluation; graphitisation.

## 1. Introduction

Coke is one of the important materials for ironmaking process such as blast furnace as it plays multiple roles by providing heat energy, performing the role of reducing agent and spacer for maintaining the blast furnace permeability. Due to increasing economic and environmental concerns, there is growing interest in reducing coke consumption by using innovative blast furnace operations such as accelerating coke reactions at relatively lower reactions. In an operating blast furnace, coke carbon structure is continuously modified as it descends towards lower parts of a blast furnace. Evolution coke carbon structure is well known to influence its reactions in a blast furnace such as solution loss reaction and graphitisation. Coke quality issues are be-

coming increasingly pertinent as less coke would be available to supply sufficient reducing gases under proposed innovative low temperature BF operations. On the hand, graphitisation behaviour could influence its fines generation behaviour in high temperature regions of an operating blast furnace. Therefore, understanding of evolution coke carbon structure at increasing temperatures is very important for the success of any new innovative blast furnace operations.

Carbon structure of carbonaceous materials is often characterized by maceral analysis or reflectance measurements which are often subjective in nature and do not distinguish atomic level differences of different carbon types. Recently, advanced analytical tools such as the X-ray Diffraction or Raman Spectroscopy are being developed to characterize carbon structure of different carbonaceous materials includ-

ing coal and their high temperature derivatives. The former gives the crystalline structure and the latter gives the bounding structure. Therefore, by comparing the XRD and Raman analysis of an identical sample, a deeper insight of the coke carbon structure can be developed. Even though many studies have been reported to use Raman spectroscopic analysis to understand the structure analysis of carbonaceous materials, the understanding of modification of coke carbon structure with increasing temperature is still far from complete particularly the interpretation of Raman analysis.<sup>1-13)</sup> Raman peak of the graphite like materials is well known to appear at  $1580\text{ cm}^{-1}$ . This Raman peak, also known as G band, is related to the energy of  $sp^2$  bonding and is assigned to the normal graphite structure.<sup>4)</sup> In less ordered carbonaceous materials, Raman peaks are often observed at  $1360\text{ cm}^{-1}$  and  $1620\text{ cm}^{-1}$ . Those peaks are known as that of D and D' bands, respectively, and are believed to originate from defect structure of graphite. But only two broad peaks appeared near  $1600\text{ cm}^{-1}$  and  $1360\text{ cm}^{-1}$  for coke.<sup>1)</sup> The peaks are designated as G\* band peak and D\* band peak, respectively. It may be noted this designation does not physically mean the graphite and its defect structure. On the basis of these peaks, several parameters have been developed to characterize the structure of carbonaceous materials. However, no universal characterizing method has yet been established for carbon materials which have widely different structure.

The structure of less ordered carbonaceous materials is considered as the mixture of graphite like structure and amorphous structure.<sup>14)</sup> Recently, various structure parameters such as crystallite height (Lc), crystallite width (La), interlayer spacing (d) of graphite like structure and proportion of amorphous carbon (Xa) have been obtained from XRD analysis.<sup>14)</sup> Often, the raw XRD data of carbonaceous materials particularly char and cokes require mathematical processing to identify various carbon peaks and to calculate these parameters.<sup>14)</sup> Figure 1 shows a typical reduced intensity curve of a carbonaceous material illustrating four carbon peaks, indexed as (002), (100), (110) and  $\gamma$ . The (002) band is generally accepted as the average stack height of the aromatic planes of carbon crystallite, while (100) band at around  $44^\circ$  ( $2\theta$ ) and (110) band at around  $81^\circ$  ( $2\theta$ ) are attributed to hexagonal ring structures. The  $\gamma$  band is usually observed in a ( $2\theta$ ) angular range of  $16\text{--}23^\circ$  and is associated with packing of the saturated structure such as aliphatic side chains or condensed saturated rings.

In the present work, an industrial grade metallurgical

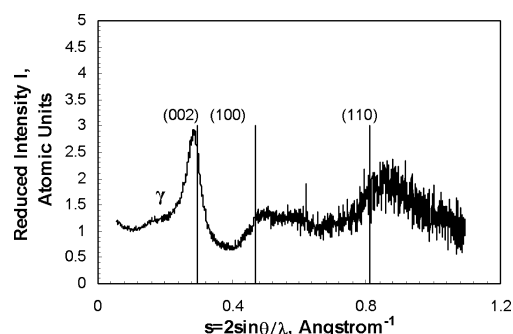


Fig. 1. Illustration of four carbon peaks in a reduced intensity curves of a typical non-graphitic carbonaceous material. Four carbon peaks are also indicated.

coke was taken as an example. The coke was thermally annealed at a range of temperatures over two time intervals. The modification of structure was followed by using the above two methods as a new approach. The X-ray diffraction analysis was carried out at School of Materials Science and Engineering, The University of New South Wales while the Raman spectroscopic analysis was conducted at the Department of Production Systems Engineering, Toyohashi University of Technology. Both XRD patterns and the Raman spectra of coke samples were obtained after annealing at different temperatures. On the basis of Raman analysis, new structure parameters were derived to evaluate the modification of carbon structure. The main aim of this study is to measure new parameters based on Raman analysis and to relate them with XRD based structure parameters in order to further improve the understanding of thermal behaviour of coke in different ironmaking processes.

## 2. Experimental

### 2.1. Sample Selection

The metallurgical coke used in this study was supplied by the Nippon Steel Corporation. The composition was fixed carbon 87.9%, ash content 11.7% and VM. 0.4%. The ash could react with fixed carbon of coke to change coke structure during high temperature annealing. Therefore, coke sample was pretreated to reduce the ash content by dipping into the 9 wt% HF aqua solution and 5 vol% HCl aqua solution at the room temperature each for 24 h. Subsequently, coke sample was washed with distilled water and dried at 413 K. After the pretreatment, the ash content was lowered to *ca.* 2%.

### 2.2. Thermal Annealing

Coke sample was thermally annealed at 1273 to 2473 K in nitrogen or argon stream. The annealing time was 5 and 20 min. Further details of the procedure are provided in a previous publication.<sup>1)</sup>

### 2.3. Raman Spectroscopy

The laser Raman spectrum analyzer (NRS-1000, made by JASCO) was used. The laser source was green laser of 532.1 nm wave length and the maximum power of 100 mW. The unit was equipped with microscope so that the analysis of micro structure was possible. The beam diameter was  $4\ \mu\text{m}$ . The power was 14 mW. The exposure time was 15 s at once and the procedure was repeated three times. The analysis was carried out on the annealed sample for 5 min.

### 2.4. X-ray Diffraction

The XRD spectra of powdered coke samples were obtained by using Siemen Powder Diffractometer. Copper K $\alpha$  radiation (30 kV, 30 mA) was used as the X-ray source while the intensities data was collected for 5 s at each step in a step-scan mode ( $0.05^\circ/\text{step}$ ) over a  $2\theta$  range of  $5\text{--}115^\circ$ . Carbon structure parameters were obtained by using recently modified technique. The modified technique was developed using MATHEMATICA application with main aim to introduce the objectivity in the curve fitting routine while maintaining the key features of the original technique as detailed in our previous publication.<sup>14)</sup> In the modified pro-

gram, an arbitrary  $X_a$  value is considered to obtain corresponding reduced intensity curve. For curve fitting, suitable segments of the curves were selected on both sides of the maximum intensity position of the peak *i.e.* avoiding any spikes or rapid curvature changes. The modified program automatically determines the centre position of the selected peak on  $\text{Sin } 2\theta$  axis by extending horizontally the extremities of these segments. Subsequently, curve fitting was carried out on both sides of the peak of the reduced intensity curve following the least-square error approach. The reduced intensity data are obtained by repeatedly trying a range of arbitrary amorphous carbon content ( $X_a$ ) until the least-squared error becomes minimum. On the basis of the identified most reasonable value of  $X_a$ , the reduced intensity curve was reproduced for subsequent data processing to calculate other structural parameters. Figure 1 shows an example of the reduced intensity curve of a typical carbonaceous sample. Most of the structural parameters were reproduced within reasonable accuracy. Due to strong sensitivity of  $X_a$  on the peak geometry,  $X_a$  values of all the samples could not be estimated particularly those of with very low amorphous carbon or high mineral content. However, the measured  $X_a$  values were sufficiently clear to reflect the modification of carbon structure during different thermal annealing conditions.

### 3. Results and Discussion

#### 3.1. Carbon Structure Evolution: Raman Analysis

Figure 2 shows the change in the Raman spectrum of coke after thermal annealing at different temperatures. Unlike graphite like materials, only two broad peaks were observed near  $1600\text{ cm}^{-1}$  and  $1360\text{ cm}^{-1}$  as seen on the top curve of Fig. 2. The vertical broken lines show the peak position of G, D and D' bands of graphite structure. Clearly the broad peaks did not accord to these G, D and D' band peaks. The former broad peak can be assigned to G\* peak, and the latter, D\* peak. Up to the annealing temperature of 1673 K, there was no noticeable change in the Raman spectrum. At 1873 K, the spectrum change slightly such that both of G\* band peak and D\* band peak became sharper. At 2073 K, the G\* band peak was split remarkably into two peaks while at 2473 K, the spectrum became similar to that of synthetic graphite.<sup>1)</sup>

Several approaches have been used to characterize carbon structure of graphite like materials with Raman spectrum analysis, namely, peak intensity ratio,<sup>5)</sup> peak area ratio<sup>6)</sup> and peak half width.<sup>7)</sup> The peak ratio of D band peak to G band peak is called R ratio,  $R = I_D/I_G$ . The R ratio was compared to the size of graphite structure of La which was determined by XRD which decreased with increasing La.<sup>5)</sup> Thus, the R ratio can be used to evaluate perfection degree of graphite structure. Katagiri *et al.*<sup>8)</sup> made the map using R ratio and half width of peak for the more precise characterization of materials. Thus, characterization method of graphite like materials seems to be well established.

On the other hand, there have been limited reports on the characterization methods of non-graphitic materials such as coal, coke *etc.* They are the similar R ratio as above, but using the D\* band width,<sup>2)</sup> the ratio of  $I_{D^*}/I_{G^*}(R^*)$ ,<sup>3,9)</sup> band separation,<sup>10)</sup> the ratio of peak to back ground<sup>11)</sup> and combi-

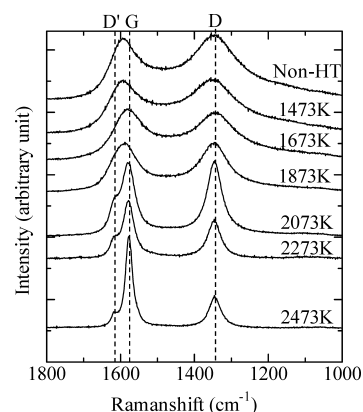


Fig. 2. Change in Raman spectrum of coke with annealing temperature.

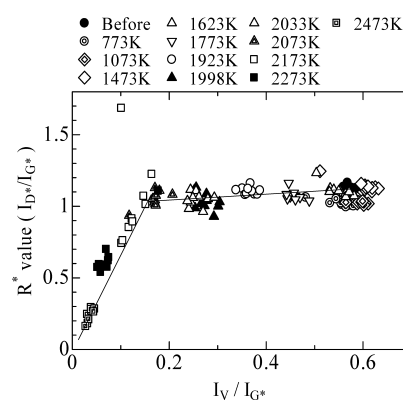


Fig. 3. Illustration of coke structure modification during thermal annealing on a  $R^*$  Value- $I_V/I_{G^*}$  plot.

nation of  $R^*$ , and  $I_V/I_{G^*}$  where  $I_V$  is the intensity of minimum point between two peaks.<sup>12)</sup> Accordingly, Fig. 3 shows the changing path of coke structure by thermal annealing on  $R^*$  Value- $I_V/I_{G^*}$  diagram. Figure 3 shows that the structural changes are clearly visible only when the annealing temperature exceeds 2073 K. However, no more detailed information can be obtained from these figures. Up till now, no universal characterization method has been established for the carbonaceous materials with widely different structure.

In the previous paper,<sup>1)</sup> new parameters which can be used for all carbonaceous materials were developed as follows. Examining the change in Raman spectrum of coke with the annealing temperature, two broad peaks of G\* and D\* become sharper at higher temperature and G\* peak splits to G and D' peak at further higher temperature. It can be seen that the spectrum can be composed of several peaks. The curve fitting with four peaks, G\*, D\*,  $R_1$  and  $R_2$  was tried, as shown in Fig. 4. In order to reproduce the experimentally obtained spectrum, it was necessary to assume additional peaks of  $R_1$  and  $R_2$ . The  $R_1$  peak appeared around  $1510$  to  $1527\text{ cm}^{-1}$  and  $R_2$ , around  $1239$ – $1280\text{ cm}^{-1}$ , respectively. These two peaks are assigned to the so-called turbostratic<sup>14)</sup> or random structure. These additional peaks are also reported on diesel soot, but the position are slightly different, namely,  $1500\text{ cm}^{-1}$  and  $1180\text{ cm}^{-1}$ . The peak position data of random structure has not been analyzed so far and will be analyzed in future.

The peak position of G, G\*, D, D' and D\* band is plotted

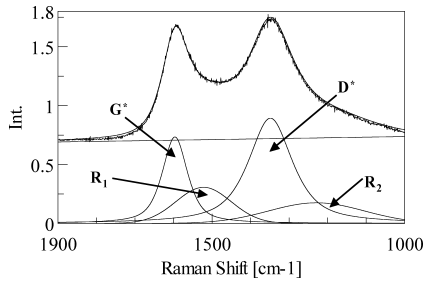


Fig. 4. Illustration of typical curve fitting of a Raman spectrum of coke with four peaks.

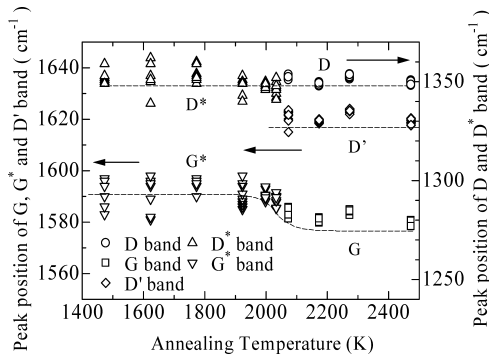


Fig. 5. Change in peak position of different bands with annealing temperature.

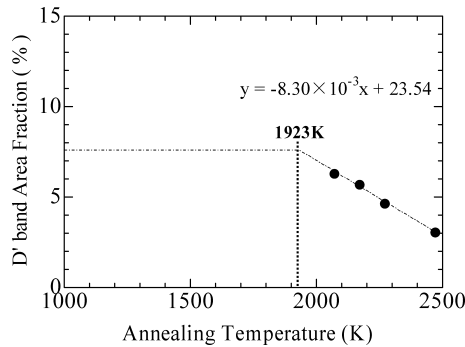


Fig. 6. Variation of D' band area with annealing temperature.

against the temperature in Fig. 5. The position of D\* and D' peak did not change with the temperature, while that of G\* changed from 1998 to 2173 K. At higher temperature than 2173 K, the peak position was constant at 1580 cm<sup>-1</sup> which corresponded to that of G band of graphite structure. At higher temperature than 2073 K, the D' peak appeared. Therefore, the G\* peak can be considered as the combined peaks of G and D'. These peaks could be identified by curve fitting at higher temperature than 2073 K. In Fig. 6, the fraction of area under D' peak to the total area is plotted against the temperature and shows that this fraction increases linearly with decreasing temperature. At lower temperature than 2073 K, D' peak could not be identified. The fraction was extrapolated down to 1923 K. At farther lower temperature, the peak position of G\* band did not change. Thus, the fraction was considered constant at lower temperatures.

On the basis of the area of respective band peak, three new structure parameters can be defined:

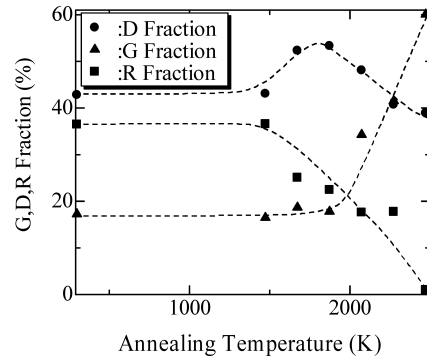


Fig. 7. Variation of D, G and R carbon fraction of coke with annealing temperature.

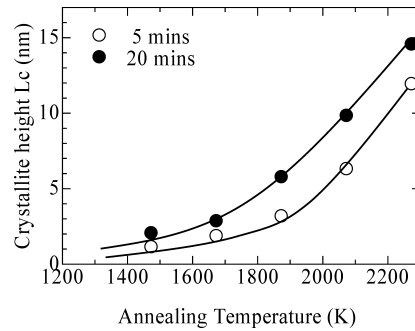


Fig. 8. Variation of carbon crystallite height (Lc) of with annealing temperatures after holding for 5 and 20 min at each temperature.

$$G \text{ Fraction (\%)} = 100(G_A/T_A) \dots \dots \dots (1)$$

$$D \text{ Fraction (\%)} = 100(D_A + D'_A)/T_A \dots \dots \dots (2)$$

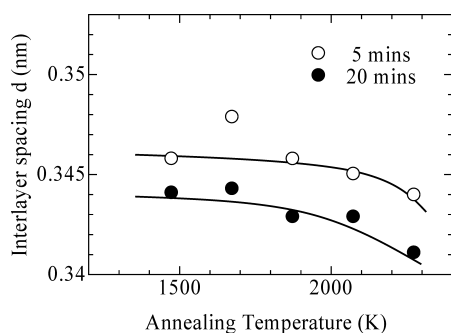
$$R \text{ Fraction (\%)} = 100(R_{1A} + R_{2A})/T_A \dots \dots \dots (3)$$

where the suffix A denotes the area of respective band peak and  $T_A$  is the total area. Figure 7 shows the variation of these new structural parameters *i.e.* G, D and R fractions of coke with annealing temperature. The R fraction decreased monotonously with the temperature from 1500 K while the D fraction increased from 1373 to 1988 K but decreased remarkably from 2033 K. The G fraction started to increase slightly from 1373 K and remarkably from 2033 K. Random structure changes to the graphite structure with many defects up to 2033 K. And the graphite grains grew remarkably when the coke sample was annealed at higher temperature than 2033 K. Therefore, Fig. 7 clearly shows that structural modification begins to occur from 1373 K, and can be clearly distinguished with the help of new parameters.

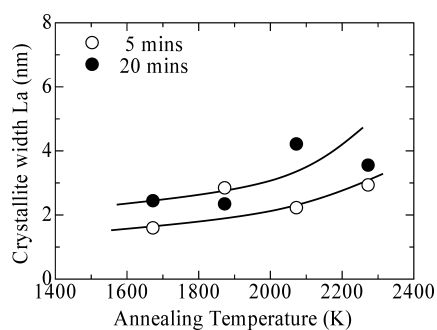
**3.2. Carbon Structure Evolution: XRD Analysis**

The structure parameters of Lc, La, d and  $X_a$  could be evaluated for the annealed samples. The reduced intensity curve of non-annealed sample was so broad that the structure parameters could be evaluated.

Figure 8 shows the variation of the carbon crystallite height (Lc) with annealing temperature. It may be noted that the Lc and La value are indicative of average stack height and average lateral dimension of aromatic planes.



**Fig. 9.** Variation of interlayer spacing ( $d$ ) of carbon crystallite with annealing temperatures after holding for 5 and 20 min at each temperature.



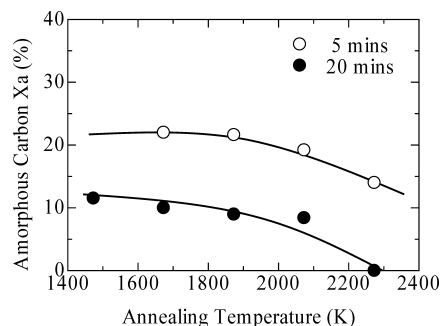
**Fig. 10.** Variation of carbon crystallite width ( $L_a$ ) of coke with annealing temperatures after holding for 5 and 20 min at each temperature.

Figure 8 shows that  $L_c$  value of coke at 1473 K after 5 min of annealing was 1.14 nm which is typical of common metallurgical coke before annealing. Initially, the  $L_c$  value increases slowly with increasing annealing temperature, however, it increases rapidly as the temperatures exceeds from 1873 to 2073 K. This relationship of increasing  $L_c$  with temperature is consistent with our previous observations.<sup>15)</sup> Figure 8 further illustrates that the  $L_c$  values also increase as the annealing duration increased from 5 to 20 min, however temporal effect was not significantly at lower annealing temperatures. The effect of annealing duration on  $L_c$  change increases as the annealing temperatures exceeds 1873 K.

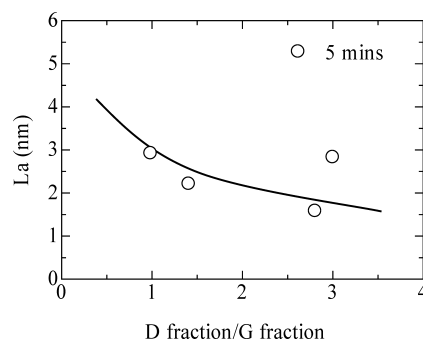
**Figure 9** shows that interlayer spacing decreases with increasing annealing temperature such that it approaches to interlayer spacing of graphite (0.335 nm) with increasing temperature.<sup>13)</sup> The results imply that coke graphitization in an operating blast furnace may not be strongly influenced by residence time which is often less than 20 min at a given temperature particularly in upper parts of blast furnace.

**Figure 10** shows that  $L_a$  values of coke did not change significantly with annealing temperature up to 1873 K. It appears that coke is experiencing *in-situ* gasification during thermal annealing as coke gasification is often associated with preferential loss of basal carbons *i.e.* decreasing  $L_a$  values. Higher values of  $L_a$  after longer duration of annealing suggest that thermal effect of stacking of carbon layers exceeds the loss of carbon removal. The  $L_c$  and  $L_a$  values were found to increase rapidly after 1873 K indicating intensive growth of carbon crystallites in all directions.

**Figure 11** shows that amorphous carbon content  $X_a$  decreases consistently with increasing annealing temperature



**Fig. 11.** Variation of amorphous carbon content ( $X_a$ ) of coke with annealing temperatures after holding for 5 and 20 min at each temperature.



**Fig. 12.** Correlation between  $L_a$  and D fraction/G fraction.

which also indicate the possibility of *in-situ* gasification due to preferential removal of amorphous carbon. The XRD analysis suggests that at temperatures less than 1873, carbon structure might be modified by loss of basal carbons while at higher temperature rapid graphitization could occur due to realignment of carbon.

### 3.3. Correlation between Raman and XRD Structural Parameters

**Figure 12** shows the relation between  $L_a$  and D fraction/G fraction. The datum at the fraction of 3 seems to jump up. This datum corresponds to that at 1873 K and 5 min in Fig. 10. It is larger than the datum at 20 min in the same figure. Thus, this datum seems to contain some experimental error. The ratio decreased as the  $L_a$  increased except the above datum. This relation is similar to that between  $L_a$  ratio and of  $R$ .<sup>5)</sup> Therefore, the D/G ratio can be similarly used to evaluate perfection degree of graphite structure. Comparison of the data of 5 min annealing from Fig. 5 with the corresponding R fraction data from Fig. 12 indicates that both started to decrease at around 1500 K. Therefore, it appears that the amorphous content as determined by XRD should have the bounding structure corresponding to  $R_1$  and  $R_2$  bands of Raman spectrum. Figure 9 shows that although interlayer spacing decreased with annealing temperature, the minimum value is larger than 0.335 nm which is the value of natural graphite.<sup>13)</sup> Figure 7 shows that G fraction increases up to 60%. But, this graphite structure does not seem to be the true graphite structure, but elongated graphite structure.

## 4. Conclusions

A metallurgical coke was annealed in a laboratory reac-

tor under a range of thermal conditions up to 2473 K. The evolution of carbon structure was characterized using Raman and XRD techniques. Following conclusions were made.

(1) The Raman spectra of most of the cokes displayed two broad peaks G\* ( $1620\text{ cm}^{-1}$ ) and D\* ( $1360\text{ cm}^{-1}$ ). Relative intensity or shape of Raman band peaks were related to lateral growth of coke carbon crystallite ( $L_c$ ), as measured by XRD, such that both did not change significantly up to annealing temperature of 1873 K. On the basis of deconvolution of broad peaks G\* ( $1620\text{ cm}^{-1}$ ) and D\*, new structural parameters G, D and R fractions were obtained to quantify graphitic, graphitic defect and random carbon fractions of coke.

(2) The XRD study indicated that the stack height,  $L_c$ , of carbon crystallite of coke increased with increasing annealing temperature while the impact of heat treatment duration was not significant particularly at temperatures less than 1873 K.

(3) The average carbon crystallite width,  $L_a$ , did not increase significantly up to 1873 K followed by a sharp increase with further rise in the annealing temperature, which could be contributed by the loss of basal carbon as a consequence of *in-situ* gasification.

(4) At the annealing temperature exceeding 1873 K, increase in  $L_a$  values was related to decrease in the D/G ratio. The study showed that lateral growth of carbon crystallite was attributed to progressive reduction of defects of graphitic carbon, and can be monitored by D fraction parameter of Raman Analysis.

(5) The amorphous content as determined by XRD should have the bounding structure corresponding to  $R_1$  and  $R_2$  bands of Raman spectrum.

(6) The study demonstrated that combined application of XRD and Raman techniques can provide a comprehensive assessment of coke behavior in a range of BF process

conditions.

### Acknowledgement

The present work was supported by the "Research Project on Innovative Ironmaking Reaction in New Blast Furnace Aiming at Half Energy Consumption and Minimum Environmental Load", Ministry of Education, Culture, Sports and Science, Japan. The metallurgical coke was provided by the Nippon Steel Corporation. A part of this work was undertaken as part of the Cooperative Research Centre for Coal in Sustainable Development (CCSD) Research Program 5.1 (Ironmaking).

### REFERENCES

- 1) M. Kawakami, T. Karato, T. Takenaka and S. Yokoyama: *ISIJ Int.*, **45** (2005), 1027.
- 2) C. A. Johnson, J. W. Patrick and K. M. Thomas: *Fuel*, **65** (1986), 1284.
- 3) S. R. Kelemen and H. L. Fang: *Energy Fuel*, **15** (2001), 653.
- 4) R. Vidano and D. B. Fischbach: *J. Am. Ceram. Soc.*, **61** (1978), 13.
- 5) F. Tuinstra and J. L. Koenig: *J. Compos. Mater.*, **4** (1970), 492.
- 6) A. Cuesta, P. Dhamelincourt, J. Laureyns and A. Martinez-Alonso, J. M. D. Tascon: *Carbon*, **32** (1994), 1523.
- 7) T. Noda, K. Miyazawa, K. Fukada and S. Itagaki: *CAMP-ISIJ*, **14** (2001), 112.
- 8) G. Katagiri: *Tanso*, **175** (1996), 304.
- 9) J. Chino, Y. Ishibashi, N. Gunji, H. Iwata, Y. Suzuki, S. Itagaki and N. Mitani: *Tetsu-to-Hagané*, **76** (1990), 34.
- 10) T. Jawhari, A. Roid and J. Casado: *Carbon*, **33** (1995), 1561.
- 11) G. Katagiri and N. Takeda: Int. Conf. on Coals and Organic Petrology, Japan Institute of Energy, Tokyo, (1996), 14.
- 12) G. Katagiri, S. Kanbara and M. Harada: Proc. of 7th Annual Meeting, Japan Institute of Energy, Tokyo, (1998), 1.
- 13) A. Sadezkey, H. Muckenhuber, H. Grothe, R. Niessner and U. Pöschl: *Carbon*, **43** (2005), 1731.
- 14) L. Lu, V. Sahajwalla, C. Kong and D. Harris: *Carbon*, **39** (2001), 1821.
- 15) S. Gupta, V. Sahajwalla, J. Burgo, P. Chaubal and T. Youmans: *Metall. Mater. Trans. B*, **36B** (2005), 385.