DEVELOPMENT OF 3D ANALYSIS METHOD OF COKE MICROSTRUCTURE USING MICRO-X-RAY CT[1]

Yuichiro Yamamoto[2]
Yoshiaki Kashiwaya[2]
Masaru Nishimura[3]
Masahiro Kubota[4]

Abstract

Recently, μ-X-ray CT was developed and used in many industrial fields. However, the in the case of application to the analysis of coke macrostructure, it is quite complicated material having a complicated pore structure, a different kind of crystalline carbon and a variety of elements in ash. In the present study, coke before and after gasification were analyzed using μ-X-ray CT. Coke sphere(20mmϕ) was gasified with the reaction gas (Ar-30%CO_2) at 1100^oC for 60min. The degree of gasification was 25.4%. Microstructure before and after gasification was analyzed by μ-X-ray CT. The condition of 3D image analysis was decided by comparing with optical microscope image of the cross section of the resin embedded sample. Comparing with the structure of pores in the resin image and μ-X-ray-CT image, it was found that the larger structure (~0.5mm) was almost the same shape. Although the resin embedded sample cannot observe the both structures before and after reaction, the μ-X-ray CT made the nondestructive observation possible. However, microstructure less than 0.5mm was difficult to distinguish. The further attempts were performed for getting an optimum condition to make clear the smaller pore and structure.

Key words: Gasification; μ-X-ray CT; Nondestructive observation

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[2] *Graduate School of Engineering. Hokkaido University.*
[3] *Kansai Coke and Chemical Co. Ltd.*
[4] *Nippon Steel Co. Ltd.*

1 INTRODUCTION

Generally, the performance of coke in blast furnace (BF) used to prefer a high strength and low reactivity, generally. One of the reasons is in the importance of the gas and liquid permeability in the lower part of BF, which are related to the stable operation of BF. On the other hand, the energy saving on the BF operation will contribute the decrease of CO_2 emission greatly, because the proportion of CO_2 emission in the ironmaking field is quite large. To decrease the RAR(Reducing agent ratio), the reaction efficiency in the BF should be increased.

In such a circumstance, researcher in Japanese research institutes are carried out many experiments not only for high strength but high reactivity of coke, extensively. However, it is recognized that the reactivity and the strength of coke contradict each other. The high reactivity coke generally has a low strength. To overcome the contradiction, we are going to use the catalytic effect on the coke gasification.

Relatively large numbers of elements (such as Ca, K, Na and Fe, and so on) are known as the catalyst[1-5] on the carbon gasification reaction.

In this series of study, Fe catalyst[6-8] was used for accelerating the gasification reaction and many kind of Fe content materials added to a coke with different ways. In such a study, it is important to clarify the mechanism of acceleration by Fe catalyst. Furthermore, the position (on the inner surface of pore or in the carbon matrix) of Fe catalyst in the coke is most important for clarifying the effect, because the reaction gas will diffuse from the surface into inside of coke through the pore. The morphology of pore and position of catalyst would affect to the effective performance of catalyst.

On the other hand, the X-ray CT (computer tomography) is using in the medical field in the last few decades. However, the resolution was not enough for using the coke analysis, because the pore size is in the order of micro-meter. Recently, the μ-X-ray CT[9] was developed and used in the industrial fields. However, the coke is quite complicated material having a complicated pore structure, a different kind of crystalline carbon and a variety of elements in ash.

In the present study, coke before and after gasification were analyzed using μ-X-ray CT. The optimum condition to make clear the coke pore structure was clarified by comparing the cross section of sample in the resin.[10-12]

Table 1. Ultimate analysis of coal. (d.a.f)

VM (%)	Ash (%)	Total S (%)	C (%)	H (%)	N (%)	O (%)
36.1	8.5	0.48	75.13	4.95	1.87	9.07

d.a.f: dry ash free

Table 2. Experimental conditions and gasification degree obtained in the present experiment.

Name	Catalyst (%)	Diameter (mm)	Reaction time (s)	GD* (%)
Sample 1	-	20.1	4200	25.4
Sample 2	2.61	20.1	4200	31.0
Sample 3	11.1	19.6	4200	31.7

*GD: Gasification Degree (d.a.f)

2 MATERIALS AND METHODS

Table 1 shows chemical composition of coal used in the present study. Table 2 shows experimental conditions and gasification degree (GD) obtained in the experiment.

Figure 1 shows the schematics of experimental apparatus. The coke sample was ground into a spherical shape with 20mmϕ in diameter, and an alumina tube (1mmϕ×10mm) was inserted in the sample as a marker for 3D analysis of CT image. Before reaction, the sample was measured by μ-X ray CT. Then the sample was moved to the reaction tube and heated up to 1100°C using induction furnace. Gasification reaction was carried out under the reaction gas(Ar-30%CO_2) for 60 min. After reaction, the sample was again measure by μ-X-ray CT. Gasification degree(GD) was estimated from the mass change before and after experiment. Porosity was measured through the image processing using a cross section of sample images obtained by the both of optical microscope and μ-X-ray CT. Reaction rate(RCS(%/min)) and gasification degree(TCS(%) ≒GD) were also calculated through the result of gas analysis obtained by QMS.

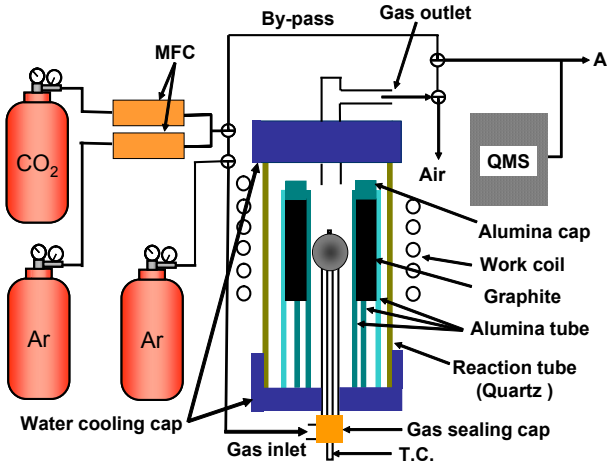

Fig. 1. Experimental apparatus.

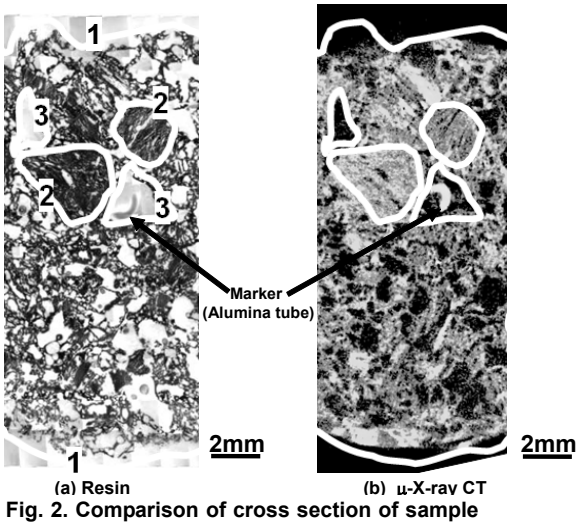

Fig. 2. Comparison of cross section of sample between resin and m-X-ray CT after reaction.

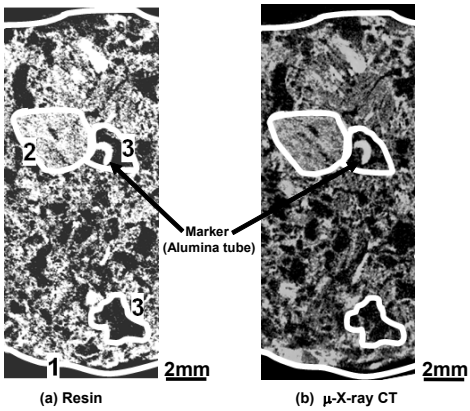

Fig.3. Comparison of cross section of sample 1 before and after reaction obtained by μ-X-ray CT.

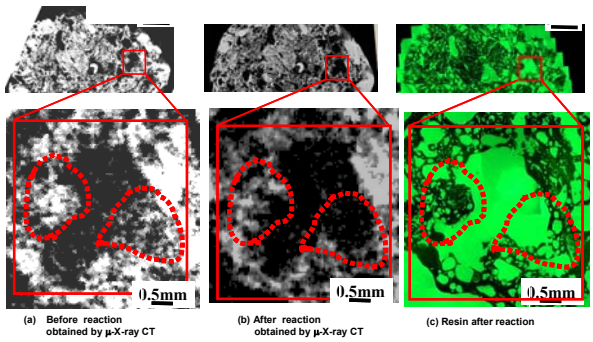

Fig. 4. Comparison of cross section of sample 1 before and after reaction.

3 RESULTS AND DISCUSSION

3.1 Comparison Between Resin Embedded Sample and μ-X-ray CT Image

(1) Problem of μ-X-ray CT image.

Figure 2(a) shows the image of cross section of the resin embedded sample after reaction. The white area shows pore and the black area shows carbon. Fig.2(b) shows the image obtained by μ-X-ray CT after reaction. In this image, black area shows pore and the white area shows carbon. The both images were obtained from the same sample (sample 1: without catalyst). Gasification degree was 25.4%(Table 2). For the convenience of comparison, some specific structures were marked with lines, which were numbered from 1 to 3 on the line. Comparing both images, the larger structure and porosity(>1mm) were confirmed in the same position, relatively easily, It was found that the minimum size for the matching between the both image was around 0.5mm in diameter for the pore and the carbon structure. The smaller structures less than 0.5mm were quite difficult to distinguish. This low resolution will be resulted from the followings;

1) Difference of X-ray absorption
   i) Thickness between the center and the periphery, which caused from the spherical shape
   ii) Thin wall thickness in the smaller structure (adsorption between air and carbon)
2) Limit of resolution of device itself

Several efforts to overcome the above problems except No. 2 are now carried out and the results will be presented in future.

3.2 Comparison of μ-X-ray CT Images Before and after Gasification

Figure 3 shows μ-X-ray CT images before and after gasification. The outline of coke is showed with a line marked as “1”, line “2” indicates the specific micro structure and line “3” indicates the pore. Comparing both images before and after gasification, it was confirmed that the structure and porosity larger than 0.5mm were approximately the same. A particular position in Fig.3 was selected and enlarged in Fig.4. For the CT image before reaction, the porosity of the CT images and resin images after reaction grew largely. By the gasification reaction with reaction gas(Ar-30%CO_2), a part of the wall structure of coke in the pore was consumed and the area of pore has spread.

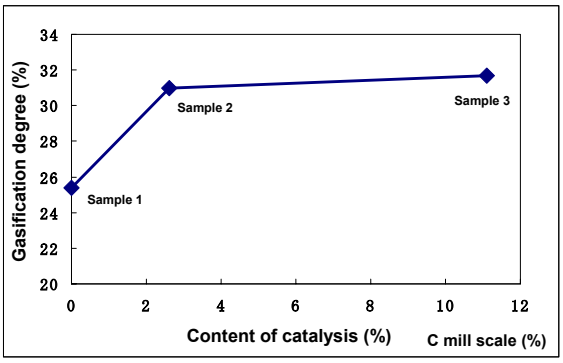

Fig.5. Variation of gasification degree.

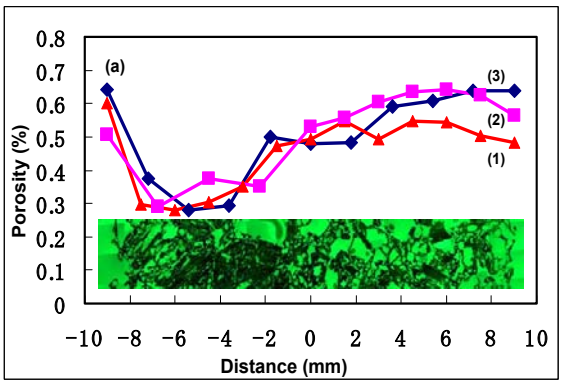

Fig. 6. Variation of porosity.
(1) before reaction using μ-X-ray CT.
(2) after reaction using μ-X-ray CT.
(3) after reaction using optical microscope.

3.3 Analysis of Coke with Catalyst

Figure 5 showed the effect of iron catalyst on the gasification reaction. The gasification degree increased with the increase of catalyst addition. However, the increase of gasification degree with addition of catalyst from 2.6% to 11.1% was only from 31% to 31.7%. It was found that the addition of catalyst more than 3% did not show the significant effect on the gasification reaction. Furthermore, a negative effect on the measurement of X-ray CT arose from the addition of Fe catalyst. From these results, it could be concluded that the adequate addition of catalyst was about 3%.

3.4 Measurement of the Variation of the Porosity from the Image Obtained

To obtain the porosity distribution from the center to periphery on the obtained images, a constant size of image was cut and the computer image processing performed for making the binary image (black and white). Then, the area of pore was counted against the total pixels for getting the porosity. In the horizontal axis, zero means the center of coke and ±10 means the both sides of coke. Fig.6 shows the porosity distribution obtained. Profile (1) in Fig.6 shows the porosity distribution of μ-X-ray CT image before reaction, the profile (2) shows the porosity of μ-X-ray CT image after reaction and the profile (3) was the one of resin embedded sample after reaction. In this case, it is an ideal condition that the porosity of resin embedded image after reaction(profile (3)) and the porosity of CT image after reaction(profile (2)) should be equal, and the profile (3) and profile (2) should be bigger than the profile (1). The result of Fig.6 became the ideal relationship. In the positions from -8 to -4 in X-axis, where the density of coke is relatively high as shown in the cut image in Fig.6, the reaction gas cannot reach to this region and the reaction degree become lowers. In the position from +2 to +8 because of lower density and high porosity of coke, the reaction gas can reach to this region. From this reason, it is considered that the reaction degree is relatively high.

4 CONCLUSIONS

In this study, the gasification experiment of coke was performed. The measurement by μ-X-ray CT for nondestructive observation was carried out. The adequate image processing condition was obtained on the basis of the cross section image of resin embedded coke. Structure and porosity of coke before and after reaction were clarified though the nondestructive observation. The obtained results are as follows.

(1) The resolution of μ-X-ray CT for coke used in this experiment was 0.5mm for pore and carbonaceous material, which caused from the difference of the x-ray absorption.
(2) The resolution decreased with the increase of iron catalyst addition.
(3) The adequate porosity distribution was obtained, when the resolution of X-ray CT image was relatively high.

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