Influence of Repetition of High-Temperature Treatment of H_2O_2-Treated Graphite on Adsorption of N_2

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Sri Lankan natural graphite previously oxidized in H_2O_2 aq.soln. was heated under a current of 1 atm N_2 at 1273K repeatedly, and was measured volumetrically for its adsorption isotherm of N_2 at 77K after each heat treatment. It was found that every isotherm was of Type II with a distinct step around a relative pressure of 0.3, and that the oftener the graphite was subjected to the heat treatment, the less the amount of N_2 adsorbed grew, and the more remarkable such a step became as well. The mesopore size distribution with Cranston – Inkley method showed that such repetition made the pores shallower. In the extreme case of the 6th treatment, the pores with radii between 1.7~ 2.0nm were almost removed, to be roughly divided into two kinds: smaller ones with a peak radius of 1.21nm and larger ones with that of 2.38nm. And besides, the t-plots for the samples demonstrated that the percentage of micropores in the surface grew larger through the repetitive heat treatment at 1273K.

Key words: Natural graphite, N_2 Adsorption, H_2O_2 liquid phase oxidation, repetition of heat treatment, porosity.

1. Introduction

There are two vital factors in the adsorption of gases onto graphite: One is the presence of various kinds of functional groups [1-3]. They are reported to attract such a polar molecule as water through hydrogen bond [4-6]. The other is the existence of pores. When the peripheries of some neighboring basal planes are secluded together, there occurs a slit-shaped pore with width several times as wide as the interlayer distance, 0.34nm[7,8]. Not only polar molecules but also an inactive molecule like N_2 or Ar is thought to easily adsorb into such pores [9-12]

In the present investigation, such natural graphite as dealt so far [6-8,12] was first oxidized in the H_2O_2 aqueous solution. Subsequently to the oxidation, the graphite was subjected to the heat treatment at 1273K several times repetitively. The N_2 adsorption isotherm was measured after each heat treatment: A distinct step always appeared around a relative pressure of 0.3 on every adsorption isotherm. It was also found that the repetition of heating at 1273K made both the adsorbed amount of N_2 smaller and the step more prominent. Of the above-mentioned vital two factors, the porosity was found more effective to the adsorption of N_2 in the present case. Now, the present authors will describe and discuss the effect of repetition of the heat treatment on the basis of the change in shape of the adsorption isotherm and the porosity of the sample.

2. Experimental

The original graphite, from Sri Lanka, is labeled G25 hereinafter in the same way as before[7,8,13], which is supplied as Graphite ACP (purity:99.5%, ash: 0.5%, particle size:1~ 30 μ m, suited to high quality small brushes, core leads, and conductive paints) from Nippon Kokuen Co. The H_2O_2 treatment was carried

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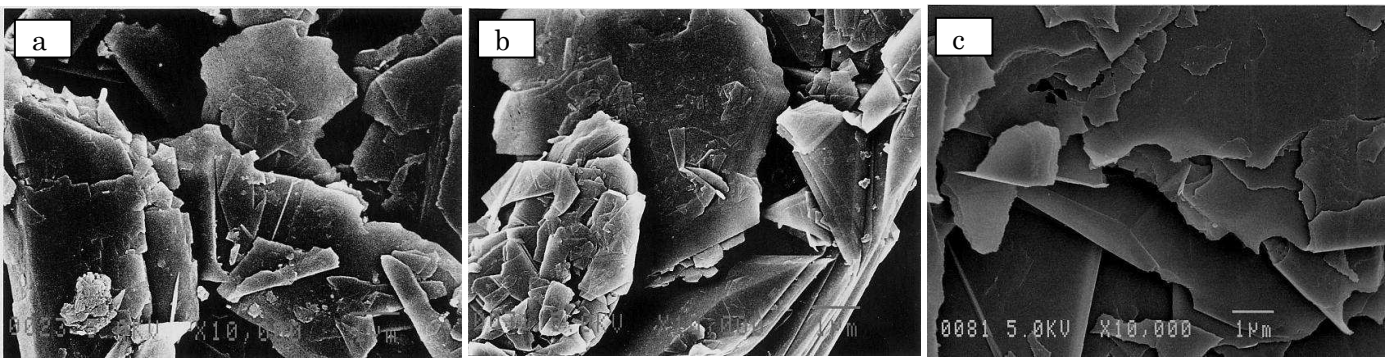

Fig.1 SEM images of graphite samples. a:G25, b:HPG25, c:HPG1000-6.　　1 μ m

out in the following way: G25 was first treated at 3073K in dry N_2 atmosphere for an hour, and then it was exposed to H_2 at 1atm at 1273K for an hour. The graphite obtained at this stage had been labeled HYG25 and used as a sample in the previous work[14]. After cooling, HYG25 was further oxidized in 31% H_2O_2 aqueous solution at 372K for an hour, to be filtered, dried at room temperature, and then stored in a silica gel desiccator. The graphite thus oxidized and stored is labeled HPG25 hereinafter. HPG25 was heated at 1273K under a current of 1atm N_2 at a flow rate of 50cm^3/min. This graphite sample was labeled HPG1000-1, and then measured for its adsorption isotherms of N_2 at 77K. After that, a set of both 1273K–heating and measurement of N_2 adsorption was carried out several times. In this report, the sample labeled HPG1000- M stands for the sample that has experienced such a heat treatment M times by then.

The adsorption isotherms were measured automatically using BEL-SORP adsorption apparatus. In the calculation of BET surface area, the cross-sectional area of N_2 at 77K is assumed[15] to be 0.162nm^2.

The gas expelled in heating HPG25 from room temperature to 1273K was analyzed quantitatively by gas chromatography and also alternately using two traps, one at 77K and the other at 195K[16]. From among the various gases expelled, the present authors focused H_2O and CO_2 for the reasons given below.

The SEM observation was carried out using JEOL JSM-890 electron microscope, the operating voltage being 5kV.

3. Results and Discussion

SEM images of graphite samples　The original graphite is powdery, and it looks like very small pieces formed in clipping off a lead of a pencil. Exactly this graphite has been used as mentioned in the experimental section.

As shown clearly in Fig. 1, little difference between G25 and HPG25 is observed, which demonstrates that the H_2O_2 oxidation scarcely affected the morphology of the graphite. Moreover, the prism planes of HPG1000-6 appear much eroded: A prominent difference is found in appearance between HPG25 and HPG1000-6. Actually, the graphite sample that experienced the heating at 1273K six times glitters in the light.

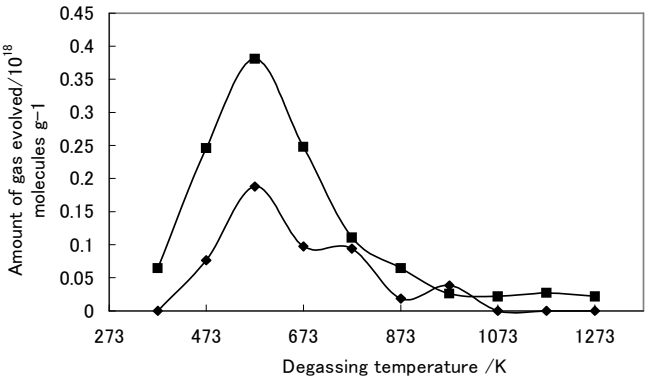

Fig.2 Amounts of H_2O and CO_2 evolved at intervals of 100K from HPG25 subjected to heating: ●: H_2O, ○: CO_2.

H_2O- and CO_2-producing surface functional groups　Figure 2 shows the temperature dependence of the amounts of H_2O and CO_2 expelled from HPG25 when it was heated for 5 h at every 100K interval of rising temperature. The liberation of those gases is a result of thermal decomposition of carboxyl, lactone, and hydroxyl groups. These functional groups are comparatively large in size and project out from the hexagonal carbon skeleton. They

probably play an important role in the formation of the slit-shaped pores in the graphite[8]. Clearly in Fig. 2, the total amount of H_2O was larger than that of CO_2, i.e., 1.21×10^{18} and 5.13×10^{17} molecules/g for H_2O and CO_2, respectively. (Both amounts were much larger compared to those expelled from HYG25, i.e., 4.34×10^{17} and 7.64×10^{16} molecules/g for H_2O and CO_2 respectively[14], which means the oxidation using H_2O_2 showed the effect of increasing such functional groups.)

Adsorption isotherms of graphite samples

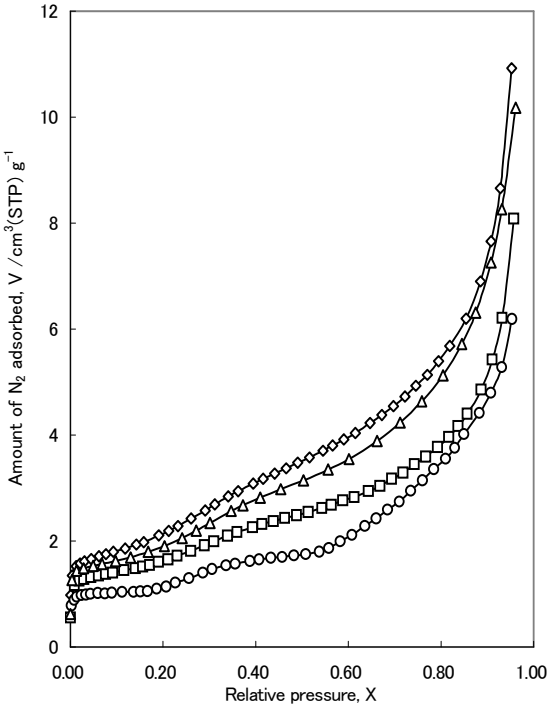

Fig.3 Adsorption isotherms of N_2 at 77K. ◇:HPG1000-1, △:HPG25, □:HPG1000-3, ○:HPG1000-6.

As can be seen in Fig. 3, the adsorption isotherm for HPG1000-1 lay slightly above that for HPG25: the first treatment at 1273K increased the amount of N_2 adsorbed on the graphite sample. The pyrolysis of the surface functional groups probably raised the adsorption capacity, as observed previously[7]. It is very surprising, however, that the adsorbed amount decreased with repetition of the heating: The shape of the adsorption isotherm on HPG1000-1 differed considerably from that on HPG1000-6.

The step appeared around the relative pressure of 0.3 on every isotherm. It probably ascribes to the formation of the 2nd adsorption layer[8]. Its shape became clearer through repetition of the heat treatment. Especially, the isotherm on HPG1000-6 in the initial part up to X=0.2 was very similar in shape to a Langmuir type, and then the adsorbed amount increased gradually after that pressure: The sample HPG1000-6 gave a unique stepwise adsorption isotherm of N_2.

The repetition of the heat treatment gradually turned the shape of an adsorption isotherm sigmoidal in this way. This fact suggests promotion of the surface homogeneity[17]. On the HPG1000-6 surface, especially, two kinds of sites seem to exist dominantly, which will be mentioned again concerning its pore size distribution.

According to Fig.4, we can see, on every isotherm, both beginning of the adsorption and steep rise in the adsorbed amount about X=0.2. At the beginning of the adsorption, N_2 molecules preferably occupy the active sites. It is found, in this sense, that the surface of HYG1000-1 was more active than that of HYG25. And moreover, the repetition of the heat treatment gradually made the surface more resistant to adsorption.

Every BET plot broke and bent downward

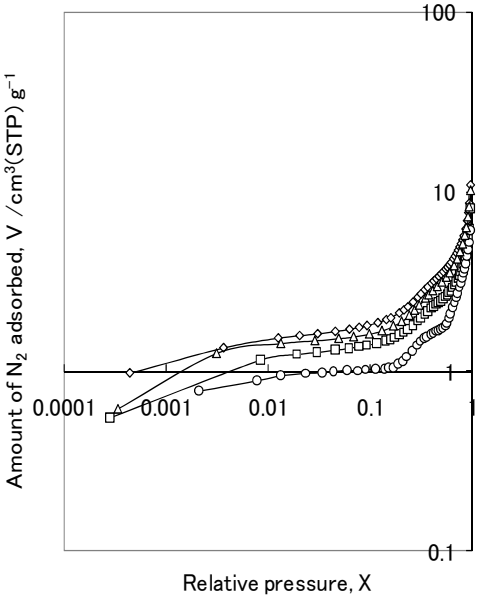

Fig.4 Adsorption isotherms of N_2 at 77K, drawn in logarithmic scale. ◇:HPG1000-1, △:HPG25, □:HPG1000-3, ○:HPG1000-6.

near X=0.2. At that pressure, the amount of N_2 adsorbed on every sample increased very steeply as shown in Fig.4. This kind of feature

Table 1 Parameters calculated from both adsorption isotherms and pore size distribution (pores < 30 nm diameter).

Sample	V_m/ml g−1	Σ /m^2g^{-1}	V_{step}/V_m	V_p/mm^3g^{-1}	A_p/m^2g^{-1}
HPG25	1.497	6.51	1.81	15.432	7.59
HPG1000−1	1.702	7.45	1.80	15.642	8.59
HPG1000−3	1.288	5.60	1.81	12.117	5.61
HPG1000−6	0.923	4.02	1.83	9.571	3.85

has not yet been explained so far though it has usually been found in the N_2 adsorption on graphitized carbonaceous materials. The present authors adopted the BET theory to the data obtained below X=0.2[8]. The surface area thus calculated decreased gradually with repetition of the heat treatment, as expected from change in shape of the adsorption isotherm. In Table 1, the values for the monolayer capacity, V_m, and the surface area, Σ, are given.

Steps in adsorption isotherms　There appeared a step around X=0.3～0.4 in each adsorption isotherm, as mentioned just above. The amount of N_2 adsorbed at the end of such step, V_{step}, was divided by V_m and the quotient V_{step}/V_m for each sample is also listed in Table 1. Values of this kind have not exceeded 2.05[8] until now. This fact strongly suggests that the step corresponds to the formation of the 2nd adsorption layer. These values in the present case are almost equal to 1.8. It is very interesting that the surface area decreased considerably, though the ratio of V_{step}/V_m is kept almost constant among all the samples. This fact means that the roughness of HPG25 surface did not change in a scale of N_2 molecular size in spite of heating at 1273K repetitively. This also means that N_2 molecules forms the 2nd layer onto the 1st one all the same way on every sample. As shown in Fig.2, the surface functional groups on HPG25 to evolve H_2O or CO_2 were small in number by nature. Therefore the prism plane is probably flat on either HPG25 or even HPG1000 series. The constancy in the quotient of V_{step}/V_m does not contradict such inherent, small amounts of the surface functional groups.

Reduced isotherms　Figure 5 is the reduced isotherm, where the surface coverage θ is expressed as a function of the relative pressure X. Theses isotherms are found slightly different from sample to sample: Each sample exactly has a different interaction with adsorbed N_2 molecules, e.g., the value of θ on HPG1000-6 near X=0 being clearly larger than

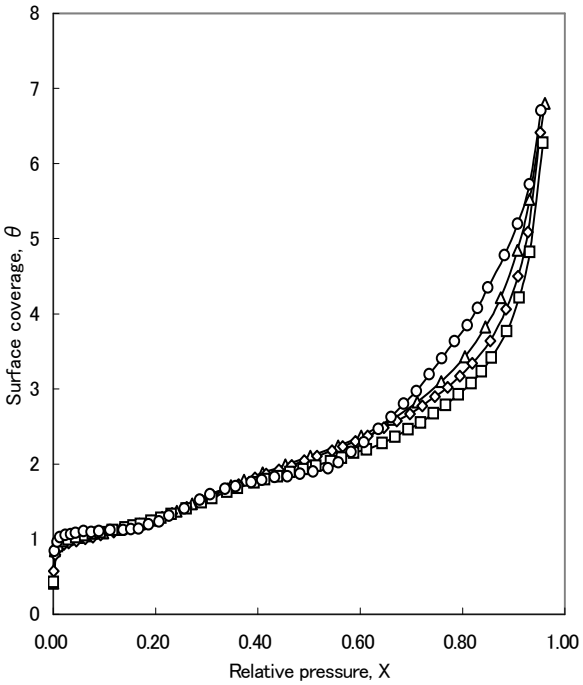

Fig.5 Reduced adsorption isotherms of N_2 at 77K. ◇:HPG1000-1, △:HPG25, □:HPG1000-3, ○:HPG1000-6.

that on HPG1000-1. Furthermore, over the region up to X=0.17, the θ value on HPG1000-6 lies above that on HPG1000-1. The isotherm for HPG1000-6 vertically rises to θ =1 at X≒0. And afterwards it is almost parallel with the abscissa of X until X reaches 0.2: Little adsorption occurs during that pressure region. Shortly after the relative pressure of 0.2, N_2 molecules a little suddenly begins to adsorb on or near the preadsorbed N_2 molecules, i.e., the appearance of the step around X=0.3, and accomplishes the 2nd adsorption layer.

In going into details, we can perceive the facts mentioned above. Taking a broad view of

the reduced isotherms, however, we can find coincidence among the isotherms until θ =3. This suggests that the adsorption proceeds almost in the same way until completion of the 3rd layer on every sample: We can infer that the repetitive heating at 1273K did not bring about a big change in the adsorption energy.

Mesopore size distributions of samples Here, we must reconfirm that the pore present on the graphite is of a slit-shaped one: The C atoms

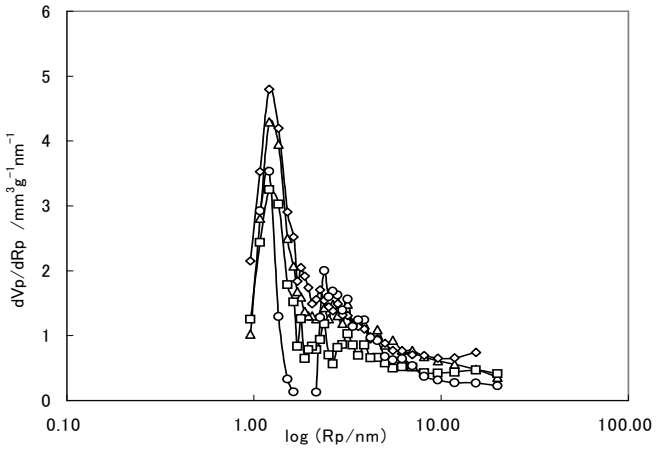

Fig.6 Distribution of pores present on graphite samples. ◇:HPG1000-1, △:HPG25, □:HPG1000-3, ○:HPG1000-6.

present on the peripheries of basal planes are so bumpy in themselves that there will inevitably be formed slit-shaped pores with its width nearly equal to the distance between two adjacent basal planes, 0.34nm. When several, neighboring sheets of basal planes are located together in secluded position, there will occur a slit-pore with its width much wider than 0.34nm. The pore size distribution of these graphite samples is given as Fig.6. The distribution curves were calculated by the classical Cranston–Inkley method[18]. All the parameters calculated from the mesopore size distribution are listed in Table 1, which also includes the monolayer capacity Vm and the specific surface area Σevaluated by the BET method and the value of Vstep that was obtained from the isotherms using a similar method of Point B[8]. The Vstep can be considered to correspond to the amount of N_2 adsorbed at the completion of the 2nd layer.

Now, it can be found that the pores developed after the 1st heat treatment at 1273K. With repetition of heating at 1273K, however, the pore volumes became smaller gradually, as given in Table 1. At last, on HPG1000-6, the pores with a radius of 1.7～2.0nm extinguished: Two peaks apparently remained on HPG1000-6, one being 1.21nm and another 2.38nm, though the distribution curves on all the other samples gave the highest peak at radius of 1.21nm alone. On the basis of such a change as observed in Fig. 5, it can be inferred that the repetitive heating at 1273K made pores shallower than before.

It is unlikely that the decrease in pore volume stems from shortening the length of the slit. If such a shortening were the case, the particle size of the graphite crystallites would become smaller that much more, and as a result, the specific surface area would be larger. As shown in Table I, however, the specific surface area actually decreased with the repetition of the heat treatment. Eventually, the decrease in depth of slit means that the surface becomes flatter than before, which is also evidence for promotion of surface homogeneity.

t-plot The information concerning the microporosity will be obtained from the t-plots given as Fig.7. For the calculations, a master

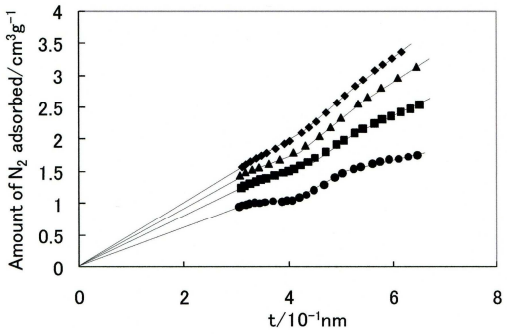

Fig.7 t-plot of N2 on graphite samples. ◆:HPG1000-1, ▲:HPG25, ■:HPG1000-3, ●:HPG1000-6.

t-curve proposed by Smith and Kasten was used[19]. It is very interesting that the plot shapes are different from those reported in the previous work[8,12] in that the slope of the 2nd straight line is smaller than that of the 1st line drawn from the origin to about t=0.33 nm. The external surface area of each sample can be estimated from the slope of its 2nd line. Table 2 lists the data calculated from these

Table 2 Parameters calculated from t-plot.

sample	Σ(BET) /m^2g^{-1}	Σ(t) /m^2g^{-1}	External Area /m^2g^{-1}	Pore* Area /m^2g^{-1}	Ratio of pore Area /%
HPG25	6.51	7.37	3.90	3.476.51	47.1
HPG1000-1	7.40	8.10	5.89	2.21	27.3
HPG1000-3	5.60	6.44	2.98	3.46	53.7
HPG1000-6	4.02	4.79	1.09	3.70	77.2

t-plots, where Σ(t) is the total surface area estimated from the slope of the 1st line, the external area being obtained from that of the 2nd line. The present authors define "the pore area" as the difference between the above two. The ratio of the pore area is obtained through dividing the pore area by the total surface area.

Each 1st line breaks about t=0.33nm. Here, we notice that the interlayer distance in graphite is 0.34nm. Hence, the area in the smallest slit increases in its ratio to the total surface with increasing cycles of heating. As mentioned above, the wider slits are considered to have decayed gradually by repetitive heating and have become shallower, which probably results in the prevalence of micropores with radii less than about 7nm. Eventually, there has occurred the enhancement of surface homogeneity.

Model of N_2 adsorption into pores Graphite, as mentioned above, has two kinds of surface planes, i.e., prism plane and basal one. The pores are of slit-shaped ones and present on the prism plane. As shown clearly in Figs. 6 and 7, the porosity actually changed from sample to sample.

As demonstrated in Table 1, the values for the cumulative surface area A_p, which is estimated from the cumulative pore volume V_p, are nearly same as those for the specific surface area from BET method Σ, and besides, all the ratioes of V_{step}/V_m stay almost the same. These facts strongly suggest that the adsorption over the middle range of pressure mainly occurs on the prism plane. Then, we can understand the process of N_2 adsorption onto the HPG samples in the following way.

N_2 molecules begin to adsorb in the slit-shaped pores to build the first layer. At the completion of monolayer, the micropores with 0.34nm wide will be filled with the adsorbed N_2 molecules, while the pores with radii larger than 1.21nm are not filled. In those mesopores, the 2nd layer will be formed above the 1st layer. At the completion of the 2nd layer, all the mesopores with radii below 1.21nm are filled with N_2 molecules: the 3rd layer will never be formed in this kind of pores. At this stage, the stacking condition of N_2 molecules adsorbed in the 2nd layer is similar to that in the 1st layer, because the slit-shaped pores are comparatively shallow. With a higher pressure region, especially, above X=0.58, all the pores with radii below 2.38nm are completely filled with N_2 molecules. The subsequent adsorption will proceed both into the pores with radii greater than 2.38nm and on the basal planes.

4. Conclusion

The amount of N_2 adsorbed increased over whole pressure range just after the first heating treatment at 1273K. Through repetition of the same treatment, the adsorbed amount declined gradually to about half of the amount on HPG1000-1. And at the same time, the step became more prominent: The 6th treatments made the isotherm of a Langmuir-type in shape during the region where X was less than 0.2, to eventually give HPG1000-6 an adsorption isotherm with a clear step as a whole.

According to the pore size distribution for these graphite samples, we can conclude that the repetition of heating at 1273K made the prism plane gradually flatter as well as more homogeneous than before. It was also found that the adsorption of N_2 over the middle pressure range occurs mainly onto the slit-shaped pores on the prism plane.

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