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Changes of Physical Properties and Crystal Sizes of Amorphous Carbon during Graphitization Process*

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Abstract

Changes of physical properties and crystal size in the graphitization process at various temperatures were examined for pitch coke as a representative material of the so-called amorphous carbon. It was shown and deduced that at about 1500°, under which temperature volatilė matters have been almost completely driven off, the growth of the layer diameter of the crystals begins and proportionately increases the thermal conductivity. Ordering of the relative orientations of each layer in a crystal begins at about 1900° causing the lowering of the electrical resistivity. The rate of the lowering of the resistivity was studied with the results indicating that the major part of the change is accomplished in the first 20 min.

I. Introduction

Amorphous carbon such as coke and carbon black is known to be transformed to graphite by heat-treatment at temperatures above about 2000° The most remarkable changes of properties before and after graphitization are found in the electrical and thermal conductivities. On the other hand, a number of experiments carried out by x-ray diffraction method have clarified that there is a wide differeuce of the crystal size between these two so-called allotropic forms of carbon. In this paper it is pointed out that there are intimate relations between the changes of the crystal size and those of the physical properties on the basis of the experimental results described below.

II. Fxperimental

Pitch coke with 0.5% ashes manufactured at The Yahata Steel Co. from coal tar and widely used for the production of the electrodes in Japan was selected as the basic material of amorphous carbon to be graphitized in the author's experiments. Particles of that coke finer than 45 mesh were mixed with coal tar (softening point 78°) produced by the same plant by the the ratio of 4 : 1 and hot-pressed in a die to the form of a circular rod under the pressure of 300 Kg/cm^2. The specimens were baked then slowly in a common-type electric furnace up to 1000° in a reducing atmosphere with the constant rate of temperature rise of about 100°/hr. A glober electric furnace was used for the successive heating up to 1300° with the same rate of temperature increase. The specimens were baked at that temper-

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ature for an hour so that they might assume stable properties. The physical properties of these samples thus prepared and finished to the desired form are on the average as follows; dimension = 30 × 5 × 5 mm³, apparent density = 1.42g/cm³, specific resistance = 8.8 Ω cm, thermal conductivity = 0.0091 cal / cm sec°C and Young's modulus = 680 Kg/mm². Each of them was subjected to the heat-treatment at different temperatures which ranged from 1500° to 2700° for successive determined time intervals in an electric furnace sketched schematically in Fig. 1.

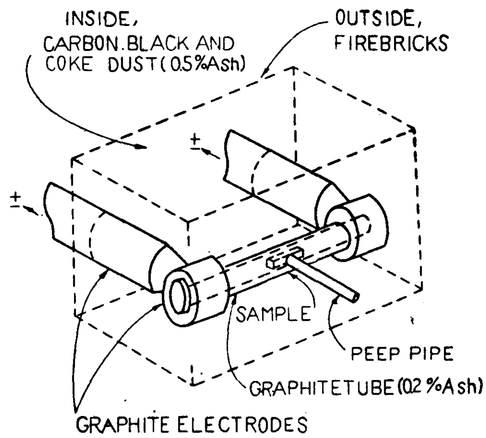

Fig. 1. Electric furnace for graphitization

The temperature was measured with an optical pyrometer and was regulated by a precise current control so that the desired temperature should be attained as fast as possible and be maintained as constantly as it could be done. In every case the rate of the temperature increase up to the desired temperature was always over about 100°/min. and the constancy was maintained in the range of about ±20°.

III. Results

Changes of electrical resistivity measured at room temperatures after each time intervals of heat-treatment at successive determined temperatures are shown in Fig. 2.

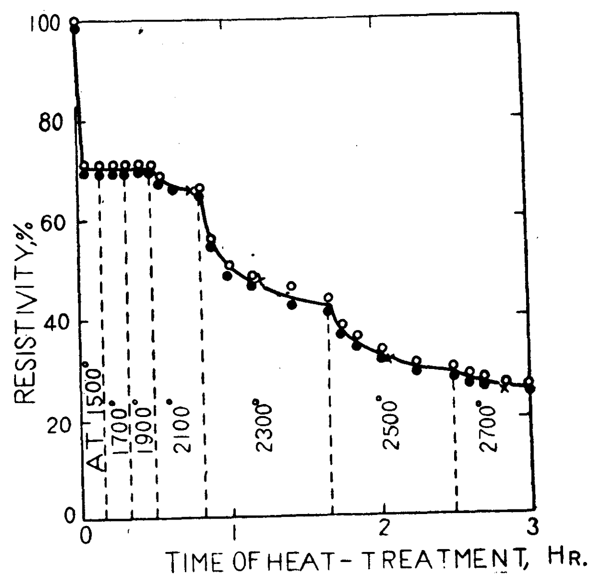

Fig. 2.

Changes of resistivity measured at room temperatures for the specimens after successive heating periods at various temperatures in an increasing oder

Herein, two specimens were subjected to the heating from 1500° to 2700°. It was made thus clear that below 1900° no lowering of the resistivity could be observed from the heating at 1500° while above that temperature the decrease sets in and each curve at a certain temperature seemes to have its own asymptotic value. The major part of the resistivity change was accomplished in the first 20 min. in any case.

Changes of various physical properties and crystal sizes measured at room temperatures after each heat-treatment for the same time interval of 20 min. at different graphitization temperatures are given in Table 1. The resistivity-temperature relations are shown in Fig. 3.

Table 1.

Changes of physical properties of pitch coke after heating for 20 min.

Heating temp.	Linear shrinkage of specimens	Density	Apparent density	Porosity	Resistivity	Young's modulus	Thermal conductivity	Ashes
C	%	g/cm^3	g/cm$_g$	%	Ω·cm	Kg/mm^2	cal/cm °C sec	%
1300	0.0	1.917	1.43	25	8.74	680	0.010	1.54
1500	1.2	2.029	1.46	28	6.32	380	0.015	1.10
1700	1.3	2.026	1.45	29	6.47	320	0.023	0.83
1900	1.3	2.033	1.45	29	6.42	270	0.034	0.59
2100	1.3	2.049	1.45	29	5.75	270	0.058	0.81
2300	1.3	2.027	1.43	30	4.20	290	0.078	0.34
2500	0.9	2.064	1.43	31	3.07	295	0.094	0.31
2700	0.7	2.111	1.42	33	2.39	235	0.140	0.24

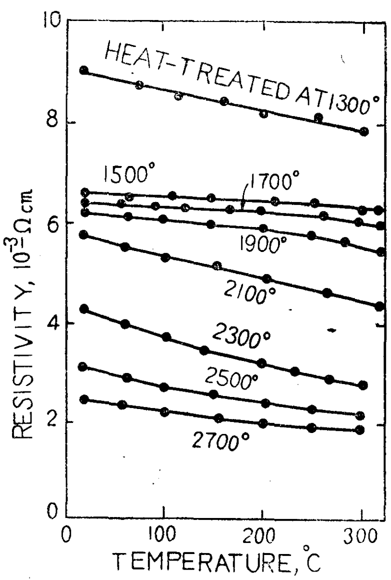

Fig. 3. Resistivity-temperature relations for the samples heated at different temperatures

Therein the electrical resistivity was measured by the potential drop method, the thermal conductivity by the Kohlrausch method, Young's modulus by the bending method and the true density was determined by the benzene displacement method.

Measurement of crystal size was

carried out by the determination of line widths of x-ray diffraction patterns by a B-type microphotometer.

IV. Discussion

There are indications[1] that before 1500°, volatile matters especially hydrogen are driven off almost completely and many experiments,[1,2] including mine, show that up to that temprature the growth of the crystals proceeds only gradually.

Therefore the large decrease of the electrical resistivity and the shrinkage of the samples indicate that up to that temperature the crystals approach each other without changing their form or size greatly, accompanied with the elimination of volatile matters situated probably at the boundaries of each layer and also in the interior of the crystals. Vacant sites produced thereby seem to correspond to the so-called 〃 Kryptoporen 〃 named by Hofmann and into which even He atoms cannot penetrate[3].

Above 1500° the specimens are composed of pure carbon excepting a small amount of ashes. In the graphitization process, however, it has been shown[4] that the ash component found usually in the raw materials used for the production of commercial carbon materials has no significant influences both on the rate of the resistivity change and on the changes of other physical properties.

Therefore, changes of the physical properties occuring in the temperature region over 1900° are solely induced by the migration of carbon atoms or in other words by the crystal growth. From this point of view, changes of the crystal sizes and those of the electrical and thermal conductivities are shown in the same figure 4 for comparison. It is a remarkabe fact that the thermal conductivity curve and that of the crystal size in the hko direction are neary parallel to each other and both show a rapid rise with temperature even in the region where the electrical

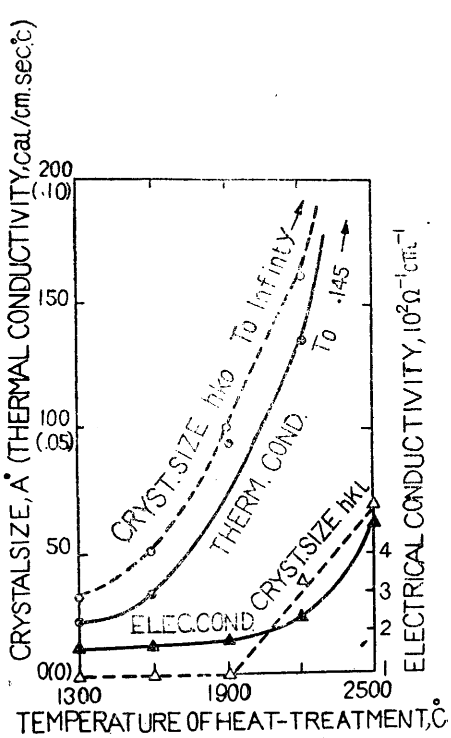

Fig. 4 Changes of crystal sizes and the electrical and thermal conductivities by the heat-treatment at different temperatures

1) H. E. Blayden, H. L. Riley and A. Taylor, J. A. C. S., **62**, 180 (1840)
2) E. A. Ragoss, U. Hofmann and R. Holst, Kolloid-Zsitschr., **98**, 118 (1943)
3) R. P. Rossmam and W. R. Smith, Ind. Eng. Chem. **35**, 972 (1943)
4) Ya. I. 01'shanskii, Doklady Akad. Nauk S. S. S. R. **62**, 489 (1946)

conductivity remains constant. Inasmuch as the hko size corresponds to the diameter of layers in a crystal, that resemblance shows that the lattice waves which carry the heat current are scattered by the crystal boundaries with the mean free path proportional to the layer diameter, as was thought by the author previously.[5]

On the other hand, the electrical conductivity seems to be determined by the crystal size in the hkl direction which has been known to represent the degree of order in the relative orientations of the layers in a single crystal. In this case, therefore, the electronic waves which carry the electric current through each layer are scattered by the irregular potential caused by the neighbouring layers. In that connection it is an interesting fact that the constancy of the resistivity during the graphitization process appeared in all tested specimens of different origin in the nearly same region of temperature and that the absolute values of tbe resistivity are approximately equal to each other if suitable corrections are made for porous nature of these carbon materials. These values are tabulated in Table 2.

Table 2.

Constant Values of Resistivity appearing during Graphitization

Origin	Apparent Density g/cm	Resistivity (uncorrected) Ω·cm	Resistivity (corrected) Ω·cm
Pitch Coke (Yahata Steel Co.)	1.45 1.54	6.4	3.6
Pitch Coke (〃)	1.54	6.0	3.6
Formaldehyde Resin	1.30	7.5	3.7
Charcoal (Cherry Wood)	0.45	16.	2.3

Thus it may be deduced that the mean value of about 3Ω.cm is a characteristic value of resistitivity for carbon materials having a complete disordered crystal structure.

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5) S. Mizushima, Phys. Rev. 82, 94 (1951)