Net Densities and X-ray Investigation of Carbon

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Abstract

Various kinds of sugar charcoals and pitch cokes, obtained by the carbonization or annealing at various temperatures and for various durations of time, were examined by measuring their net densities and by means of X-rays.

The question whether amorphous carbon represents a third modification of carbon or whether it is only finely divided graphite was first examined by P. Debye and P. Scherrer[1] by means of X-ray diffraction. All specimens were found to give diffraction patterns consisting of diffuse lines or bands. As the positions of the bands on the photograph were roughly indentical with those of certain lines of the graphite pattern, they concluded that the so-called amorphous carbon was nothing but graphite consisting of very fine crystallites. The next investigation on the same field was made by G. Asahara[2], who examined 35 different specimens of graphite and amorphous carbon by using tungsten radiation, and came to the same conclusion, viz., that amorphous carbon had the same lattice form as graphite and was not the third modification of carbon. Recently T. Watanabe[3] examined the carbon obtained from carbon monoxide; and Y. Oshima and Y. Fukuda[4] examined coke and charcoal by X-ray diffraction, coming to a similar conclusion. More recently M. Miwa[5] investigated various forms of carbon by means of cathode ray diffraction and agreed with the view that amorphous carbon was simply microcrystalline graphite.

Another group of investigators O. Ruff, Schmidt and Olbricht[6] inclined to the view that amorphous carbon was a "para-crystalline state" of matter bridging the amorphous and crystalline states more effectually than what is known as the "mesomorphic" or liquid crystal state. G. L. Clark[7] by means of the X-ray diffraction method and chemical considerations deduced the conclusion that the "para-crystalline state" actually existed. N. K. Chaney and his co-workers[8], from their investigations of the absorbing power of active carbon divided amorphous carbon into Alpha and Beta modifications. Recently P. Rishnamurti[9] and P. C. Mukherjee[10] examined sugar charcoal, an active

carbon and Ascheson graphite, by means of X-rays, and obtained the result that the lattice constant of the amorphous carbon was larger than that of ordinary graphite.

In the present investigation the writer measured the net densities of various carbons subjected to varied heat treatment, in parallel with the X-ray examination. It is most important that the material used in the experiments should be absolutely pure. Kahlbaum sugar which was first caramelled at 195°C. was put in a platinum crucible and was then charred in muffle electric furnace at various temperatures for 3 hours. The net densities of the fine powders of the specimens thus charred at various temperatures were measured by the method devised by U. Yoshida and B. Takei[11], which is especially suitable for obtaining net densities of porous and powdery substances. To get a general idea of the relation between the carbonizing temperature and the net densities, the results were plotted (Fig. 1), the net densities of carbon as ordinates, and the carbonizing temperatures as abscissae.

Table I

Graphite		Electrode Carbon					
		No. 1		No. 3		Carbonized at 880°C.	
θ (glancing angle)	Intensity	θ (glancing angle)	Intensity	θ (glancing angle)	Intensity	θ (glancing angle)	Intensity
6° 1′	W	6° 6′	W				
9° 36′	m						
10° 4′	S						
11° 21′	m	11° 19′	S	11° 19′	W	11° 9′	band S
12° 4′	S	12° 35′	S	12° 35′	S	↕	
13° 14′	S	13° 26′	S			13° 3′	
15° 30′	VW	15° 33′	VW	15° 33′	VW		
16° 46′	m	16° 48′	W				
17° 53′	S						
18° 4′	m						
18° 17′	m						
19° 43′	W	19° 20′	W	19° 20′	W		
20° 27′	VW						
20° 48′	VW	20° 47′	VW				
21° 53′	S	21° 43′	m	21° 43′	m	21° 12′	W
		24° 22′	m				
		26° 50′	W				

As is evident from the curve thus plotted, the net density of carbon increases as the carbonizing temperature is raised. With 250°C. charcoal (by which is meant charcoal carbonized at 250°C, a similar notation being employed for the higher carbonizing temperatures) and 300°C charcoal the presence of the sugar composition was tested by Fehling's solution, but no traces were found. On comparing the net densities of these two charcoals with that of 400°C. charcoal, a sudden increase with the carbonizing temperature was observed. This change, being very important, will be fully discussed later in conjunction with the results obtained from X-ray photographs.

In the same way the sugar charcoal (whose net density was 1.537) and pitch cokes (whose net density was 1.561) were annealed at various temperatures for 3 or 6 hours. The net densities of these specimens were also measured, and the relation between the annealing temperature and the net densities is also represented in Fig. 1.

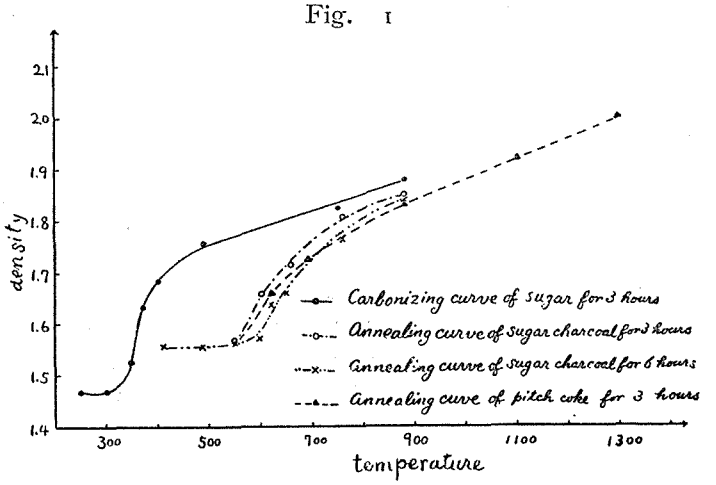
It seems to be evident, from the curves thus drawn, that the net density of carbon annealed at a given temperature is only increased

Sugar charcoal

Carbonized at 400°C.		Carbonized at 350°C.		Carbonized at 290°C		Carbonized at 250°C.	
θ (glancing angle)	Intensity	θ (glancing angle)	Intensity	θ (glancing angle)	Intensity	θ (glancing angle)	Intensity
11° 9′ ↕ 13° 3′	band S	9° 45′ ↕ 13° 3′	band S	7° 53′ – 10° 51′	band S	8° 21′ ↕ 9° 29′	band S
21° 12′	W	21°	VW				

very slightly with increase of the annealing time; and the net density of carbon annealed at a given temperature takes nearly a value which is characteristics of the annealing temperature. This fact means that the so-called "Graphitierungsgrad" is nearly a constant for a given annealing temperature.

Fig. 1



As is evident from the curves in Fig. I, the net density of the carbon prepared by carbonization increases very rapidly with the carbonizing temperature when the latter exceeds 350°C. approximately, and that of the specimen annealed also increases very rapidly when the annealing temperature is higher than about 600°C.

On the other hand, some of the specimens of known net densities were examined by means of X-rays generated from a Shearer tube having a copper target. The results obtained with various specimens are tabulated in Table I. In order to compare the quality of the electrode carbon two different specimens No. 1 (whose net density was 2.211) and No. 3 (whose net density was 2.069) which were annealed at about 2500°C. and 1400°C. respectively were also examined. The glancing angles θ measured on the photographs for various diffraction lines or bands are given in Table I. It is seen clearly, from the diffraction photographs, that the interference line become sharper as the net densities increase, and the smaller the net densities the more diffuse the lines. With the 250°C charcoal there could not be found any ordinary lines observed with the specimens carbonized at temperatures higher than 400°C., but only a diffuse band appeared at $\theta = 10°$. Of course this small angle scattering also occured in the case of 880°C. and 400°C. charcoal.

Fig. 2

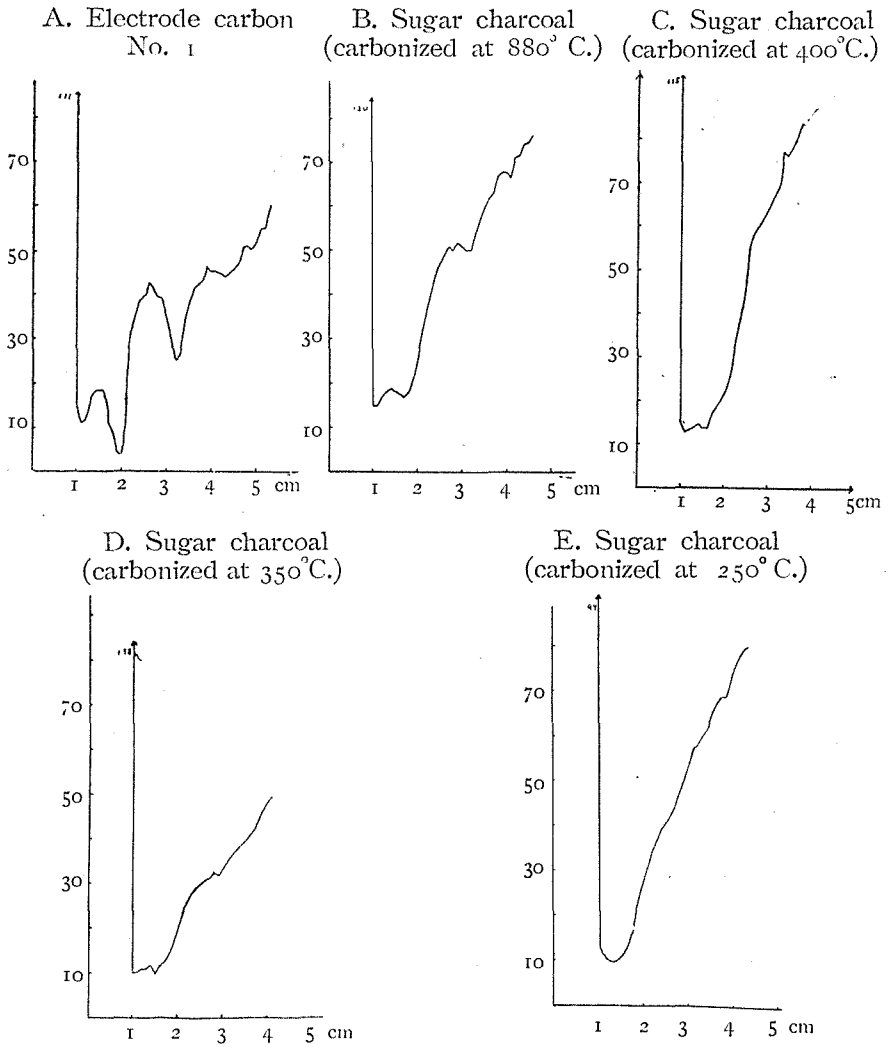
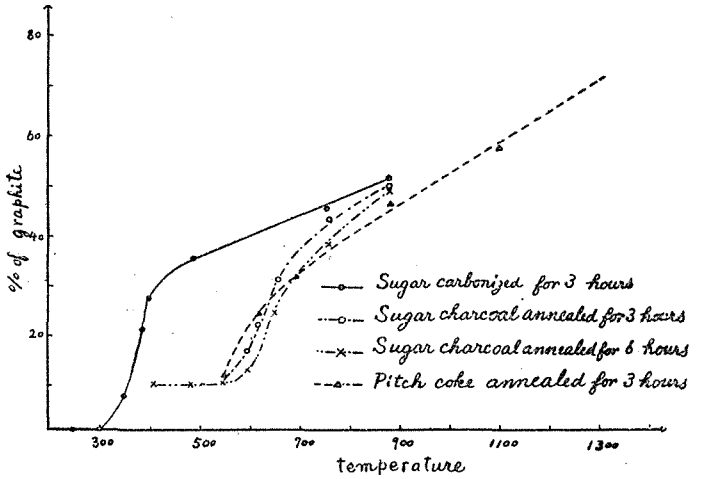


Fig. 2 shows microphotometer records of some of the specimens. The difference in the X-ray photographs between 250°C. and 400°C. charcoal corresponds clearly to the difference in the net densities between the two. As already mentioned the 250°C charcoal was confirmed to contain no sugar composition by means of the Fehling's solution.

Thus it may be concluded that the net density of the so-called amorphous carbon (whether amorphous or fine crystalline state other

than graphite is undecided) is equal to 1.475 and that the ordinary carbon is a mixture of this amorphous carbon and graphite whose net density is equal to 2.268. The weight percentages of the graphite content in the mixtures are shown in Fig. 3. It will be clearly seen that these curves in Fig. 1 are similar to those of Fig. 3. This result agrees well with that obtained by the X-ray examination.

Fig. 3



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