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X-Ray Diffraction Study of Heat-Treated Graphitized and Ungraphitized Carbon

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Heat treatment of graphitized and ungraphitized carbon samples was carried out in air and argon atmosphere from ambient temperature to 700°C. The changes in degree of amorphousness, mean crystallite size and interlayer separations were studied employing x-ray diffraction. The results revealed an increase in crystallinity when graphitized carbon was heated to 100°C and above. This enhanced degree of arrangement is indicative of the removal of residual impurities entrapped during the production processes. In ungraphitized carbon, the transition from amorphous to crystalline character was not observed upon heat treatment.

Key Words: Graphitized and ungraphitized carbons; Heat treatment; XRD

1. Introduction

Franklin[1] divided carbonaceous materials except diamond into graphitized and ungraphitized. Graphitization involves displacement and rearrangement of small groups of planes to achieve three dimensional ordering. In graphitized carbon the elementary crystallites are mobile with weak crosslinking. In graphitization, non-organized carbon is consumed first and then the incipient graphitic structure commences. In non-graphitizable carbon, cross linking develops between neighbouring randomly oriented elementary crystallites resulting in a rigid, immobile mass being formed. From the investigations of carbonaceous adsorbent preparation using different raw materials, it has been observed that the differences between graphitizing and non-graphitizing carbon are not limited to their crystallographic structure, but are also demonstrated by other properties such as magnetic susceptibility, the optical properties and the concentration of unpaired electron[2−3]. The use of these materials as adsorbents, catalysts and catalyst supports and chromatographic column packing is well documented[4−11]. It is known that thermal treatment produces the structural changes in these materials. The adsorbent and catalytic properties of these materials are enhanced with the increase in ordered structure or crystallinity. The aim of the present work was to study the structural modifications in graphitized and ungraphitized carbon as a result of thermal treatment.

2. Experimental

2.1. Materials

Graphitized carbon PGC-220-224 received from Department of Chemistry, University of Edinburgh, UK was used as such. It had powder density=0.242/ml; particle size=180-250μm and specific surface area=103m^2/g.

Ungraphitized carbon PGC-230 received from Department of Chemistry, University of Edinburgh, UK was used as such. It had powder density 0.40g/ml; particle size 100-300μm and specific surface area=575m^2/g with 0.25% ash content.

2.2. Heat Treatment of Samples

Samples of both graphitized and ungraphitized carbons were heated for 30 minutes in a resistance furnace from 100°C to 700°C. One set of samples was heated in air, while the second set subjected to heat treatment in argon atmosphere.

2.3. X-ray Diffraction Measurements

XRD patterns of virgin as well as heat-treated samples were recorded on a Phillips PW1450/70 diffractometer equipped with PW1390 channel control goniometer supply. An argon-filled proportional counter used as a detector was linked to a PW1373 rate meter and channel analyzer. CuKα 0.15418 nm radiation was generated using a Phillips PW1730 X-ray generator operated at 40kV and 30mA. Powdered samples were pressed into pellets on a hydraulic press (25kN) before XRD measurements.

3. Results and Discussion

The crystallinity data for untreated graphitized carbon includes percent crystallinity 5.53, along with 0.62nm and 0.41nm mean defect size and interlayer separation respectively. X-ray diffractograms of graphitized carbon heated in argon and air atmosphere are reproduced in Figures 1 and 2 respectively The diffused halos appearing at low 2θ values i.e., 13 to 24 degrees are indicative of the amorphous nature of material having some degree of arrangement (crystallinity) in the molecular chains[12]. The triangular peaks observed in the diffraction patterns point to the presence of crystallinity[13], which was quantified by Johnson's method[14]. The expression used for calculating the percent crystallinity is as follows:

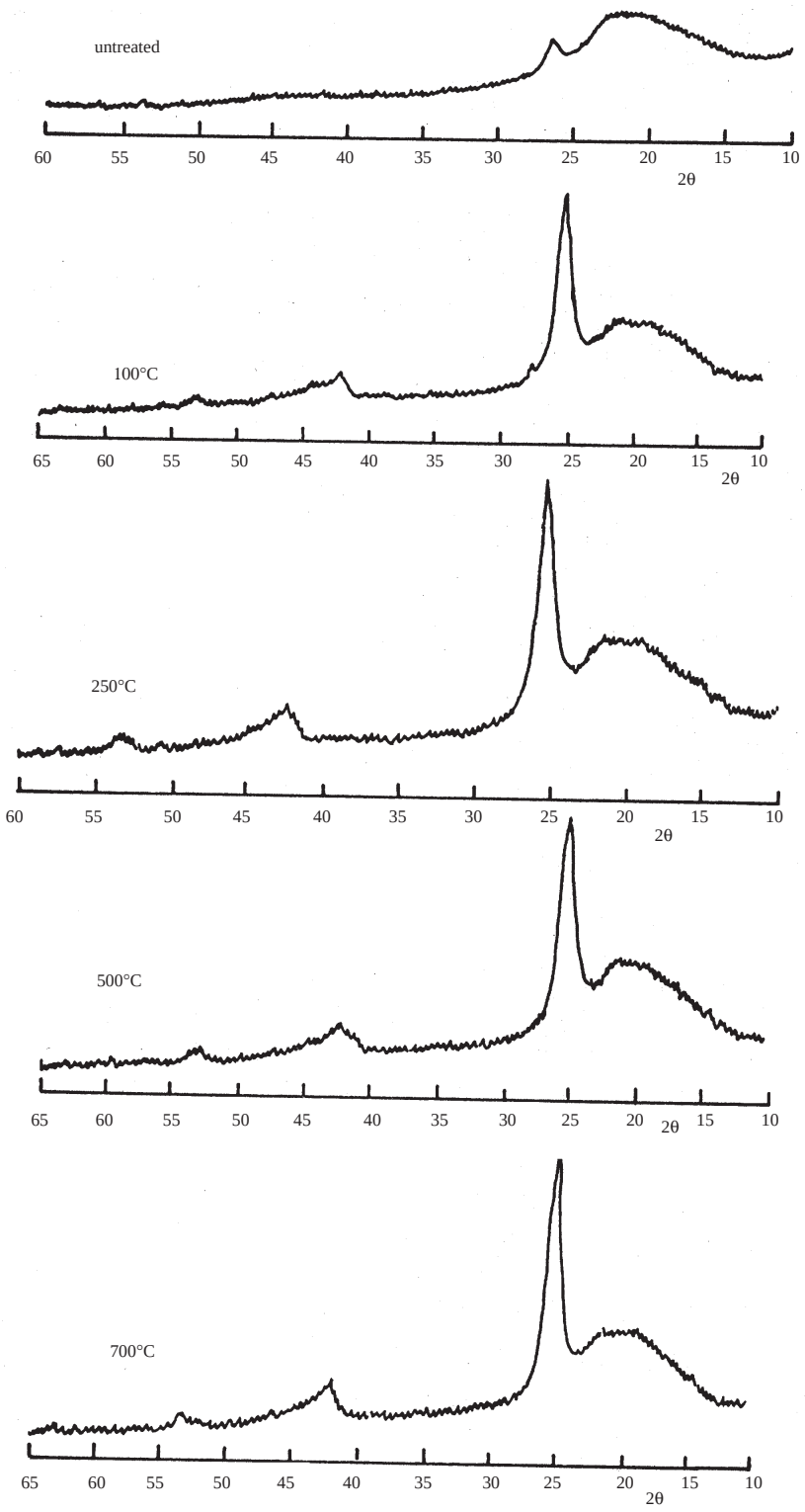

Figure 1. XRD spectra of graphitized carbon heated in argon atmosphere. [voltage=40 kv, current=30 mA, range=2000 counts

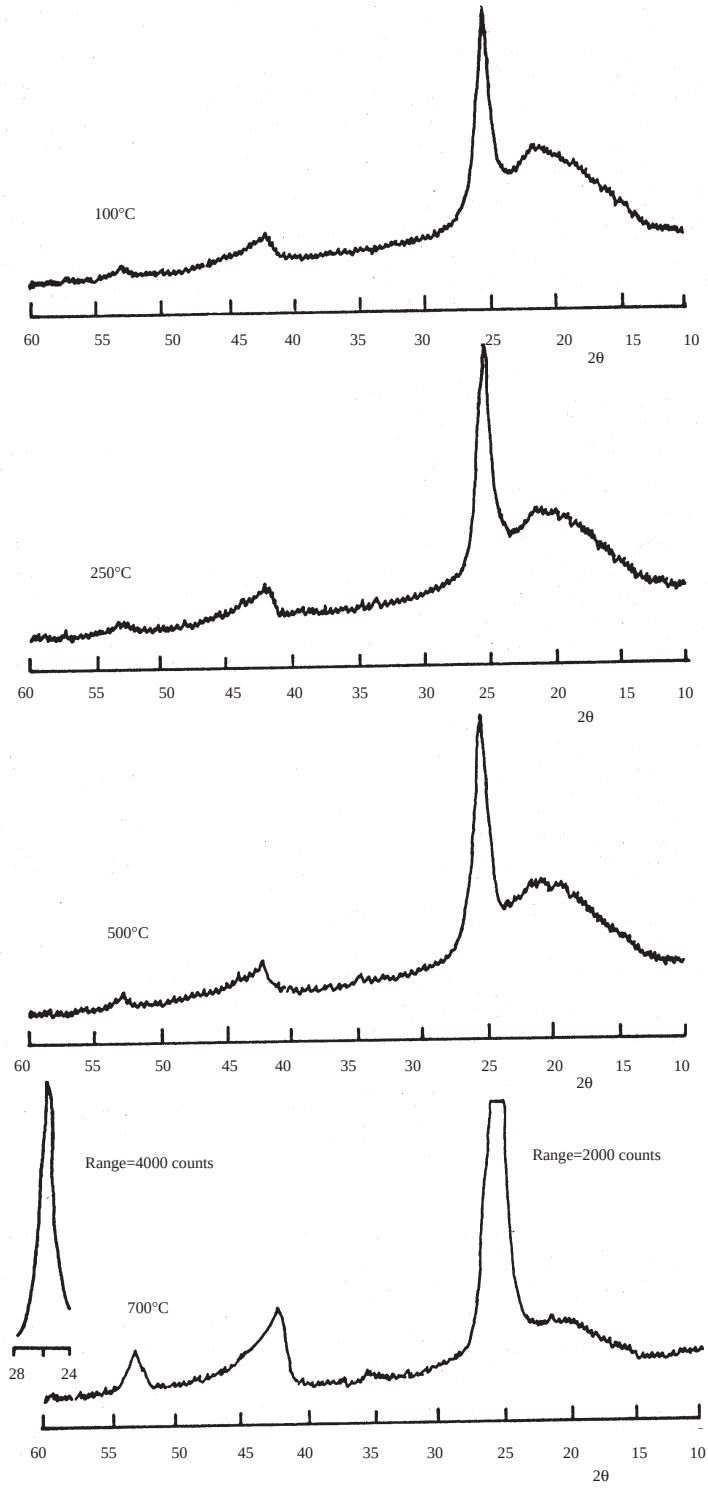

Figure 2. XRD spectra of graphitized carbon heated in air. [voltage=40 kv, current=30 mA, range=2000 counts

$$\%Crystallinity = I_C/I_A + K.I_A$$

where I_C and I_A are the integrated intensities of crystalline and amorphous peaks respectively. K is a constant taken as unity[14]. Areas of the peaks were determined by the "Cut and weigh" method. The results

are presented in the Table. It is evident from these results that when graphitized carbon is heated, the degree of order increases markedly. This effect is more pronounced for samples heated at 100°C in air than in argon. However, the overall change in percent crystallinity is comparable in both the treatment methods.

The mean defect size (Lc) was calculated by Short and Walker's method[15] using the expression:

$$Lc(nm) = 57.3K\lambda/\beta\cos\theta$$

where K is Scherrer's constant (0.87). β is peak width of maxima at half height (2θ). The tabulated results (Table) show an increase in mean defect size with the rise in temperature. It is a known fact that Lc is a function of crystallinity[16], therefore with the increase in crystallinity the mean defect size of crystallites in the graphitic layers also increases. Hence, these results also compliment the data reported for crystallinity in this paper.

The interchain separations (R) measured from 2θ values at which intensity of diffuse halos is maximum using the following expression show no significant changes.

$$R(nm) = 5/8.(\lambda/sin\theta)$$

Table Structural parameters of graphitized carbon determined by XRD.

Temp.°C	% Cryst (Air)	Lc (nm) (Air)	R (nm) (Air)	% Cryst (Ar)	Lc (nm) (Ar)	R (nm) (Ar)
100 (G)	9.32	0.75	0.51	7.73	0.71	0.54
250 (G)	9.82	0.76	0.52	8.82	0.72	0.54
500 (G)	9.82	0.78	0.52	8.83	0.75	0.55
700 (G)	9.90	0.82	0.52	8.86	0.77	0.55

$$Where\ G = Graphitized\ carbon,\ \ Ar = Argon\ atmosphere$$

The increase in crystallinity upon heat treatment in graphitized carbon can be attributed to the removal of residual impurities entrapped during the production process. The resultant movement of an individual atom or single carbon ring causing the filling of the voids, improves the perfection in existing crystallites[1,17]. Lack of significant changes in the inter layer separation can be explained on the basis that less porous and soft structure of graphitized carbon contains a large number of graphitic layers, which are already oriented parallel to one another[17].

The XRD patterns of ungraphitized carbons heated in air and argon are reproduced in figures 3 and 4 respectively. These figures reveal no appreciable changes in the degree of amorphousness in the samples. Furthermore, no transition to crystallintiy was observed even at higher temperatures. This can be attributed to the fact that in ungraphitized carbon, the number of parallel graphitic layers change very little and the rigid and immobile microporous mass is preserved even at high temperatures[1−3,17].

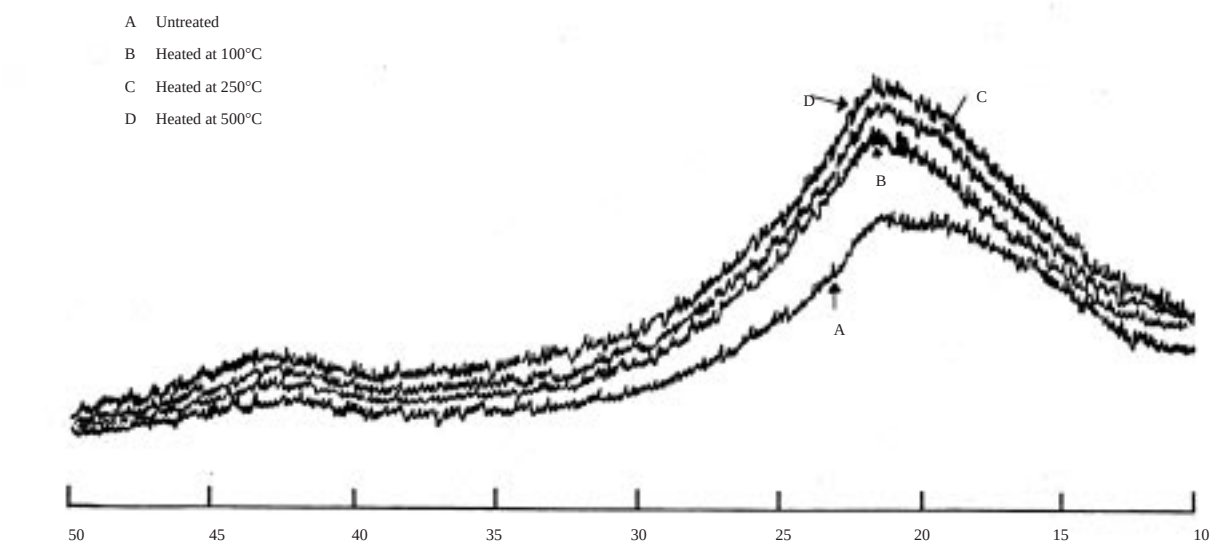

Figure 3. XRD spectra of ungraphitized carbon heated at different temperatures in air.

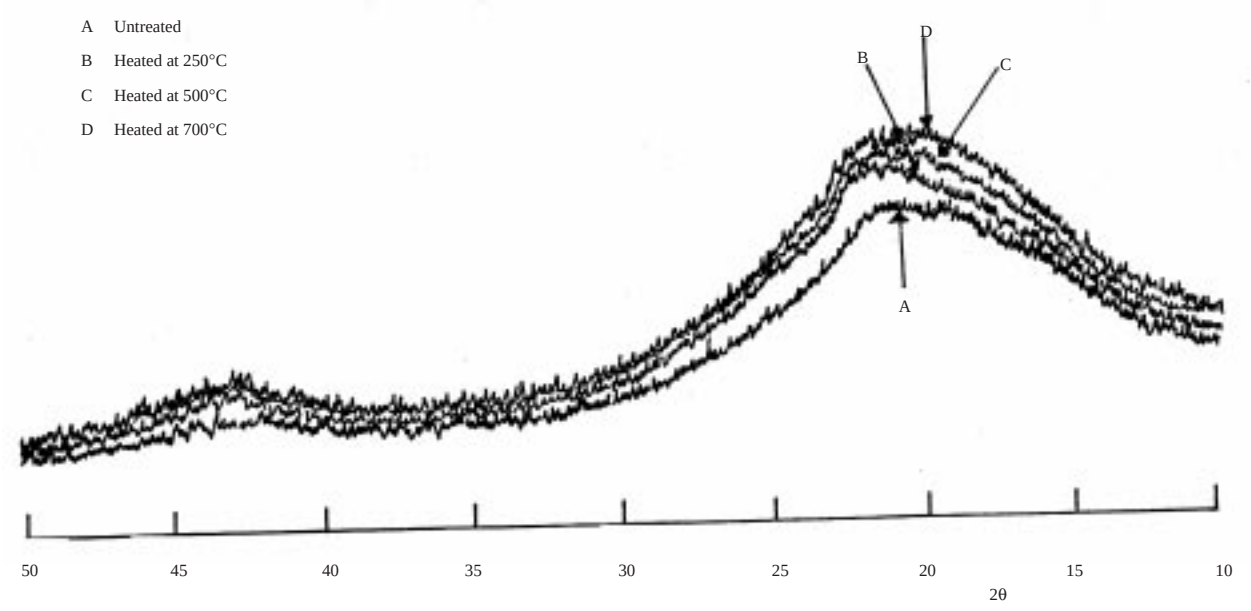

Figure 4. XRD spectra of ungraphitized carbon heated at different temperatures in argon atmosphere.

4. Acknowledgement

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