The specimens were untreated coiled-coil filaments used for the manufacture of gas-filled lamps. The increase in resolution of the a doublet with increase in temperature can be clearly observed. This series has been used with considerable success for ascertaining the likely annealing conditions in instances of filaments for which observations of the actual heat treatment are not available.

(c) Directional orientation in rolled sheet. The significance of the directional orientation of the crystallites produced in metals as a result of deformation by cold work is illustrated by the following examples.

For certain electrode parts of cathode ray tubes a deep-drawing operation is performed on rolled sheet consisting of a copper-nickel alloy containing 20 per cent nickel. Experience has shown that there are considerable variations in behaviour between different batches of metal. Whilst in certain batches the metal deformed quite uniformly over the required depth other specimens were unsatisfactory owing to formation of 'ears'. Back reflexion X-ray photographs of the two types of sheet are shown in Fig. 10. These show that



Fig. 10. Back reflexion X-ray photographs of Cu/Ni sheet revealing differences in directional orientation of the crystals. (a) Sheet with satisfactory properties. (b) Sheet with unsatisfactory properties

whilst in the satisfactory specimen there is completely disordered orientation of the crystals marked directional orientation exists in the unsatisfactory material, revealed by the concentration of the diffraction rings in certain special directions. In some instances a heat treatment of the unsuitable metal enables the random orientation condition to be achieved, but in others, possibly where the directional orientation is too far advanced, heat treatment merely emphasizes the preferred orientation of the crystals. Where non-directional orientation of the crystallites is required it is necessary

to pay close attention to the rolling schedule so that sufficient intermediate heat treatments may be given to destroy the 'fibreing' before it becomes too marked.

The second example is concerned with the manufacture of molybdenum sheet(9). If a rolling procedure is adopted in which after a partial reduction in thickness of the original ingot the rolling direction is changed by 90°, a peculiar type of brittleness is developed in the finished sheet by the final annealing treatment. The sheet is particularly weak in directions at 45° to the directions of rolling and Fig. 11 which shows a typical specimen that has been through a sand blasting process reveals in a striking manner how readily the material is fractured in these directions by mechanical treatment. X-ray examination proves that directional orientation of the crystals has been produced Fig. 11, Sample of in the sheet closely approaching molybdenum sheet the ideally preferred condition; cleavage planes, in this case the cube faces, are at 45° to the directions of rolling and at the same



rolled in two directions at right angles showing 45° brittleness

time perpendicular to the plane of rolling. When the sheet is obtained by rolling continuously in one direction this type of brittleness is not experienced, because, as X-ray analysis shows, there is considerable deviation from the preferred condition about the direction of rolling.

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THE STUDY OF CARBON BY THE DEBYE-SCHERRER METHOD

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ABSTRACT. The technique of taking Debye-Scherrer photographs of various modifications of carbon using standard 9 cm. and 19 cm. cameras of the Bradley type is described.

The method of using the curves from a manually operated null deflexion microphotometer of the Dobson type to calculate the crystallite dimensions of the carbons is explained, in which a new definition of line broadening is used. The variations in crystallite dimensions of different carbons calculated on the new basis are included. A brief account is

given of the advantages of using the 10 cm. diameter camera to show details which are completely lost when the 9 cm. diameter camera is used,

INTRODUCTION

MANY unique and interesting problems are presented by the various modifications of carbon. There have been, however, very few X-ray researches in this immense field, particularly on the so-called 'amorphous' varieties and on the structure of coal and coke. This neglect is quite understandable. A few Debye-Scherrer photographs of coals are quite sufficient to discourage a study of this very fascinating subject; the broad diffuse diffraction haloes with the numerous superimposed impurity lines do not seem to offer much encouragement for the investigator. A considerable amount of purification and chemical analysis for an accurate characterization of the materials is often required before a profitable study can be made. This necessitates close co-operation between physicist and chemist, without which progress in this field is likely to be very slow indeed.

In this paper, it is intended to outline some of the features in the X-ray technique and the results obtained. We shall deal here with some of the so-called 'amorphous' carbons, coke and coal, and mention some of the features of natural and artificial graphites as revealed by the Debye-Scherrer method.

THE APPARATUS REQUIRED

In order to make a complete X-ray study of carbon by the powder method, two sizes of Debye-Scherrer camera are preferable. These are cylindrical cameras of 9 and 19 cm. diameter respectively. The specimen, which for carbon is in the form of a fine cylindrical rod between $\frac{1}{3}$ and $\frac{1}{2}$ mm. in diameter, is at the centre of the camera, while the film, 3 cm. wide, goes on the flanges round the camera periphery. The cameras used are exactly the same as those described by Bragg, Bradley and Sykes(1). The specimen is accurately centred in the camera by an adjustable holder(2). With alloys, the specimen is continuously rotated during the exposure period, but this is quite unnecessary with 'amorphous' carbons and any line broadening attributable to specimen wobble is obviated.

The smaller camera is most suited for the study of carbons with a very small crystallite size, ranging up to 30A. For the larger crystallites, the larger camera is to be preferred. This camera also gives the high resolution required for the study of natural graphites. The choice of camera size is not governed by the width of halo alone, but by the exposure time, and some sort of compromise has to be reached in order to get sufficient important results in a reasonable period. For photographs of the very highest quality the X-ray beam is monochromatized by reflexion from a rock salt crystal and the camera is evacuated (3). An X-ray tube with a cobalt target proves to be most satisfactory. The radiation should be carefully filtered with an iron foil 7/10,000 in. thick. Peak kilovoltages greatly in excess of 40 kV should be avoided in order to cut down the background level produced by the 'white' radiation.

After taking the Debye-Scherrer photograph for a crystallite size determination, the film must be microphotometered to get an estimate of the line broadening. It is at this stage of the work that the greatest precautions are necessary. It is the author's opinion that the most suitable microphotometer for the purpose is a manually operated null-deflexion instrument incorporating a photocell of the vacuum type coupled to a Lindemann electrometer. The film density of blackening can then be *read directly* from the position of a graduated grey wedge which transmits as much light on to the photocell as does the film. A balance is obtained by means of a reciprocating shutter which allows light transmitted through the film, or alternately through the wedge, to fall on to a slit placed immediately over the cell while simultaneously moving the wedge along. Using a slit corresponding to an area of film 4 mm. high and o_2 mm. wide, the haloes are traversed in steps of o_2 mm., while the background, which varies slowly, is photometered at 1 $\cdot o$ mm. intervals. The film densities are plotted on a large scale on co-ordinate paper after the photometer readings have been taken down with the aid of a junior assistant. The whole process is very rapid. A manually operated instrument to take film 300 mm. long was constructed by the author. The Dobson type of microphotometer (Cambridge Instrument Co., Ltd.) is built on similar lines, but to take a shorter length of film.

Modern high speed double-coated X-ray film suffers from the coarseness of the grain. The long slit has the advantage of evening out the graininess. For the graphites which give sharp spectra, the slit width is cut down to 0.1 mm. and the photometry intervals in traversing the lines is also reduced to 0.1 mm.

Every film which is to be photometered is given a series of intensity calibration marks along the edge by means of a rotating sectored wheel. The steps are even, each subtending an angle of 10° , giving equal increments of exposure to the film. The calibration marks are photometered and a correction curve is constructed. The exposure of the film should be such as to keep the intensity of the haloes on the linear portion of the calibration curve, otherwise the departure from linearity must be carefully corrected for if the crystallite size calculations are to have any meaning. 'Ilfex' film with Ilford Blue Label Developer has given the author excellent results. A typical photometer curve is shown in Fig. 1. This is replotted on to a flat background before the calculations are made.



Fig. 1. A typical microphotometer curve for coke $(\frac{1}{12}$ th full scale). Usually only two haloes are visible, namely (0002) and (1010) from which the crystallite dimensions in the *a* and *c* directions can be calculated. Reproduced by permission from the Journal of the Chemical Society

The technique for making the powder specimen is quite simple. After sieving the powdered material through a 350 mesh sieve, the powder is damped with a very dilute solution of seccotine in water. A thickwalled glass capillary tube with a bore between $\frac{1}{2}$ and $\frac{1}{2}$ mm. and approximately 3 cm. long is pressed down on to a little heap of the damp powder, which is forced 92

and the line

up into the capillary. A length of steel piano wire, carefully trued at the ends and nicely fitting, is pushed down each side of the tube to compress the powder into a rod and to squeeze out the excess moisture. The resulting rod is then pushed out of the tube on to a glass plate and gently dried for a few minutes in an oven. For best results, the glue solution should be quite fresh, or the specimens will be too fragile to mount. The piano wire must just slide down the capillary and it is a good tip to use a trace of oil to lubricate the wall of the capillary tube if the carbon rod shows a tendency to jam. Hold the wire firmly in a pair of heavy pliers close to the tube and push firmly, otherwise the wire will kink badly and fail to slide down the tube. Canada balsam, so often used for making alloy specimens, is not to be recommended, as it gives a very strong halo comparable with the (0002) reflexion from 'amorphous' carbons and completely ruins the photographs.

THEORETICAL DETERMINATION OF THE CRYSTALLITE SIZE

It was shown by P. Scherrer(4) that when monochromatic X-rays of wave-length λ fall on a randomly oriented mass of crystals, the diffraction maxima become broadened when the particle size is very small. The determination of the crystallite size from the broadened line proceeds in four steps: (i) The measurement of b, the half-peak width of an unbroadened line in the position of the maximum of the broadened halo. (ii) The direct measurement of B, the total half-peak width from the broadened halo. (iii) The calculation of the amount of line broadening β from B and b using the Jones method. (iv) The calculation of the crystallite size from β . It has been shown by Scherrer and several others that the angular broadening β at the half-peak value is given by the expression

$$\beta = k\lambda/(\epsilon \cos \theta),$$

where ϵ is the linear dimension of the particle normal to the diffracting planes, θ is the Bragg angle and k is a constant of the order of unity (5). The Laue (6) method of measuring line width by dividing the integrated intensity by the maximum height of the line is to be preferred, i.e.

Half-peak width =
$$\int I d\chi / I_{max}$$
.

This definition gives due consideration to the contribution the smallest particles in the aggregate make to the basal width of the line.

In the Jones method (7), the unbroadened half-peak width b for particles of infinite size (i.e. > 1000 A) is interpolated for the position of maximum of one of the diffuse haloes. A graph relating the ratio β/B to b/B is drawn. After B is found, b/B is calculated and the graph is then used to evaluate β/B . The true diffraction broadening is then easily obtained as

$\beta = (\beta/B) \cdot B$.

With carbon it is possible to measure b directly by using a graphite > 1000 A in size. Provided the experimental conditions are the same and the specimens are made in the same way, it is sufficient to take a separate Debye-Scherrer photograph to determine b, and thus avoid having a mixture of sharp and broad lines on the same film. It has been shown by the author(8) that the laborious calculations of Jones can be avoided by the use of a simple artifice. The curve connecting β/B and b/B can be obtained to a sufficiently high degree of accuracy by taking the root mean of the ordinates of the circle

$$(\beta/B)^2 + (b/B)^2 = 1$$

 $\beta/B + b/B = \mathbf{1},$

and plotting these values against b/B (Fig. 2). This is equivalent to defining the line broadening as

$$\beta = \{ \sqrt{B^2 - b^2} \cdot (B - b) \}^{\frac{1}{2}}.$$



Fig. 2. Jones' curve for the derivation of the amount of line broadening (β)

Curve (i)
$$\left(\frac{\beta_w}{B}\right)^2 + \left(\frac{b}{B}\right)^2 = I$$
; Curve (ii) $\left(\frac{\beta_s}{B}\right) + \left(\frac{b}{B}\right) = I$;
Curve (iii) $\frac{\beta}{B} = \sqrt{\left(\frac{\beta_w}{B}\right) \cdot \left(\frac{\beta_s}{B}\right)}$.

A summary of the results of crystallite size measurements for various carbons is given in Fig. 3. The values have been recalculated from the figures originally published by the author (9), (10), (11), using the new definition of β as described above. These show interesting points of difference in the growth of carbon crystallites according to the origin of the raw materials. One of the most remarkable features of the curves is the sudden growth in the *c*-dimension of Turraun peat carbons above 700° C. The break-up or 'decrepitation' of the carbon crystallites from anthracite followed by a steady growth on further heating to higher temperatures should throw further light on the nature of the coal substance. A further discussion of this phenomenon and the glass-like nature of coke will be published elsewhere.

Another interesting phenomenon revealed by the crystallite size determinations is the variation of the a and c lattice parameters. As the *c*-dimension grows, the *c*-parameter decreases, while the *a*-parameter increases with *increasing a*-dimension (Fig. 4). The atomic volume remains almost constant throughout these changes (10).

It was mentioned above that the 19 cm. diameter camera was most suitable for the study of crystallite sizes above 30 A (8). It will also reveal subtle differences in the X-ray spectra of macrocrystalline graphite which are easily missed in the photographs from the 9 cm.



Fig. 3. Summary of results of crystallite size measurements for various carbons



Fig. 4. Crystallite size in c- and a-directions

camera. For example, the high order reflexions from natural graphites arising from the (hkil) planes are not perfectly sharp. Artificial macrocrystalline graphites, such as Acheson graphite, exhibit a series of sharp {(hkio) and (oool)} and fuzzy (hkil) spectra indicating some form of slip within the crystals in a manner analogous to the random shearing of a pack of cards.



Fig. 5. Debye-Scherrer photographs of graphites. (19 cm. camera, Co $K\alpha$ radiation.) (a) Artificial graphite from Resistor Bed, (b) Ceylon graphite [note blurred high order (hkil) reflexions], (c) Acheson (artificial) graphite [note 'extra' reflexion persists near blurred (2021)]. Photographs one-third full size

This state of affairs seems to exist in natural graphites also, but on a much smaller scale. Extra spectra which are not due to impurities also make their appearance(12), and the (0004) reflexion seems to consist of two lines (Fig. 5) and does not fall exactly in the correct position. These anomalies are being studied with the 19 cm. camera and it may be necessary to use an even larger camera (35 cm. as described by Bradley) in order to show fine details. It seems fairly certain from these preliminary observations on the Debye-Scherrer spectrum that some revision of our present ideas on the crystal structure of graphite is indicated.

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AN X-RAY EXAMINATION OF MECHANICAL WEAR PRODUCTS. BY H. J. GOLDSCHMIDT, M.Sc. AND G. T. HARRIS, B.A., Research Department,

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ABSTRACT. Powders produced by abrasion of steels in a wear-testing machine were collected and subjected to X-ray examination. The abrasion products consisted of mixtures of the parent metal (ferrite) and iron oxide. The oxides observed were FeO and Fe₃O₄, but never Fe₂O₃. Small amounts of cementite Fe₃C were also present in certain cases. The relative amounts of a-iron, FeO and Fe3O4 in the wear powder depended characteristically on the composition of the steel, its phase constitution, and certain experimental factors. The method is illustrated by its application to a series of carbon steels. The amount of a-iron and the types and amounts of oxides present are indicative of the temperature attained during wear when the known phase relations in the iron-oxygen system are utilized. One aspect of the wear process is considered as being in effect a localized short time heat treatment and 'quench' of both the original and abraded test material.

INTRODUCTION

This paper is primarily intended to draw attention to what is believed to be a new approach to the problem of mechanical wear or abrasion under unlubricated conditions in air, and to serve as an example of how X-ray methods can usefully be applied to a technical problem of great complexity.

The mechanism of wear has never been fully established, owing to the large number of factors controlling the phenomenon. Thus the wear resistance of a solid, in contrast to other physical properties, is affected by

such factors as surface finish, melting point, and humidity of the surrounding atmosphere, while other factors, such as hardness, which might be expected to exert a strong influence, do not appear to do so.

The method of attack has been to collect the fine powders produced by the abrasion of iron and steels and to subject them to X-ray analysis. Mathews(1) used X-ray methods to investigate wear products, but his back-reflection photographs only led him to conclude that by wear 'the crystal structure can be completely broken down to the basic dimensions, indicative of severe stressing during sliding contact'. No conclusions were possible regarding the phases present.

EXPERIMENTAL TECHNIQUE

A wear-testing machine (Avery-Brownsdon) was used in which a revolving wheel of hardened and tempered high speed tool steel is forced under constant load against a plane sample to be tested, wearing in it a groove whose length is a function of the wear resistance. The tests were run without any lubricant and the fine powder formed by the abrasion was collected and examined in a 9 cm. diameter Debye-Scherrer powder camera. The wheel had a radiused periphery and thus as wear proceeded the area of contact increased and the pressure dropped; during the first few seconds of the run the pressure was of the order of 7 kg. per sq. mm.,