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### Effect of Pre-exposure to Artificial Pressure on the Surface Area of Anthracite

RECENTLY, M. I. POPE and S. J. GREGG<sup>1</sup> have examined the effect of pressure (applied at room temperature using a hydraulic press) on the *n*-butane surface area of powdered vitrains, ranging in VM (d.m.f.) from 16.3 to 43 per cent. They find that the effect of a 4 kilobar (kb) pressure depends upon the rank of the vitrains. For vitrains containing 37 per cent VM or greater, pressure decreases the surface area; for higher rank vitrains, pressure increases the surface area.

It was of interest to determine whether their conclusions could be extended to higher rank coals and to higher applied pressures. Consequently, in this study the effects of pressures of 5 and 40 kb on the N<sub>2</sub> (78°K) and CO<sub>2</sub> (195°K) surface areas of a -200 mesh Pennsylvania anthracite [94.5 per cent carbon (d.m.f.) and 5.0 per cent VM] were examined.

The pressure treatment consisted of holding for one hour at room temperature 1.0 g samples in a hydraulic press. Application of pressure did not result in any significant particle agglomeration. Adsorption isotherms were determined volumetrically using a conventional apparatus. Prior to a run, each sample was outgassed at 125°C for 12 h. One hour was allowed for each adsorption point. Specific surface areas were calculated using the BET equation, taking the cross-sectional areas of N<sub>2</sub> and CO<sub>2</sub> as 16.2 and 20.0 Å<sup>2</sup>, respectively.

Table 1. Effect of pre-exposure to artificial pressure on the surface area of anthracite

Pressure, kb	Surface area, m <sup>2</sup> /g	
	N <sub>2</sub>	CO <sub>2</sub>
~0	32	210
5	33	204
40	52	222

Table 1 summarizes the surface area results. For the three samples, the CO<sub>2</sub> surface areas are very much larger than the N<sub>2</sub> surface areas. This has been previously noted for both bituminous and anthracite coals<sup>2-4</sup>. From adsorption results on zeolite molecular sieves<sup>5</sup>, this difference in N<sub>2</sub> and CO<sub>2</sub> adsorption can be taken to mean that the samples have a significant surface area in pores between *ca.* 4 and 5 Å. That is, N<sub>2</sub> at 78°K can get into 5 Å openings rapidly but only slowly into 4 Å openings<sup>5</sup>. In contrast, CO<sub>2</sub> at 195°K can get into both 4 and 5 Å openings rapidly<sup>5</sup>.

Compaction at 5 kb produced a negligible change in the N<sub>2</sub> and CO<sub>2</sub> areas. Compaction at 40 kb produced a negligible change in the CO<sub>2</sub> area but, by contrast, produced a significant increase in the N<sub>2</sub> area. The exposure of a brittle solid, such as anthracite, to high compacting pressures would be expected to produce internal cracking (macropores) within the anthracite particles. It is suggested that these macropores cut across the micropores,

thereby decreasing the average diffusion length into the micropores. The result would be an increase in  $N_2$  adsorption in the 4 to 5 Å pores, when the adsorption time is held constant. The fact that a compaction pressure of 5 kb did not produce a change in  $N_2$  area suggests that negligible (additional) internal cracking was produced under this pressure. This could be a result of the fact that previous grinding of the anthracite to -200 mesh had already produced a greater degree of internal cracking than that normally produced by compaction at 5 kb. That is, F. DACHILLE and R. ROY<sup>6</sup>, who followed the effect of grinding on phase transitions in minerals, find that grinding can expose a solid to intermittent point-contact pressures as high as 20 kb.

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### Topography of Kish Crystals and the Effect of Oxidation in Air

DETAILED studies have been reported recently on the production of etch pits in purified Ticonderoga natural graphite crystals as a result of oxidation in oxygen in the temperature range 700°-870° C<sup>1,2</sup>. Others have also been concerned with the effect of oxidation on the topography of natural graphite<sup>3-6</sup>. In this communication, the effect of oxidation on the topography of purified kish crystals is considered.

Kish is a waste product which forms on the surface of molten iron of high carbon content during the manufacture of steel. It is carbon which has been taken into solid solution with the iron and is afterwards evolved when the iron cools. Kish particles are large and flaky, resembling large particles of natural graphite. Walker and Imperial<sup>7</sup> have previously shown that purified kish has the same interlayer spacing as Ceylon natural graphite, indicative that it has a large crystallite size and essentially complete three-dimensional ordering.

The kish used in this investigation was purified by boiling alternately in hydrochloric acid and hydrofluoric

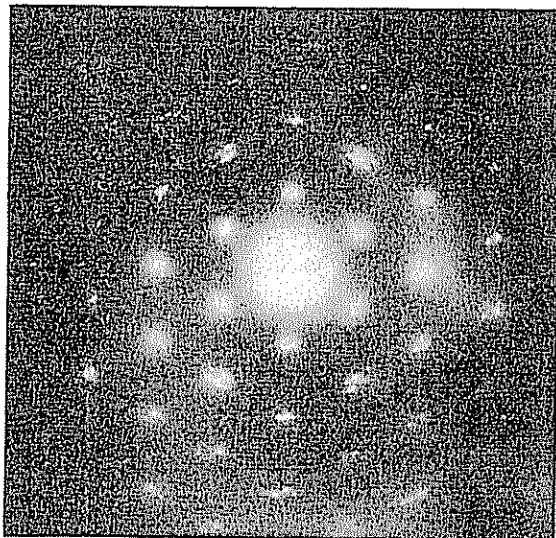


Fig. 1. Transmission electron diffraction pattern of purified kish



Fig. 2. Basal plane (0001) surface of kish purified in hydrochloric acid. Twin bands run parallel or intersect at 60°. ( $\times$  c. 200)

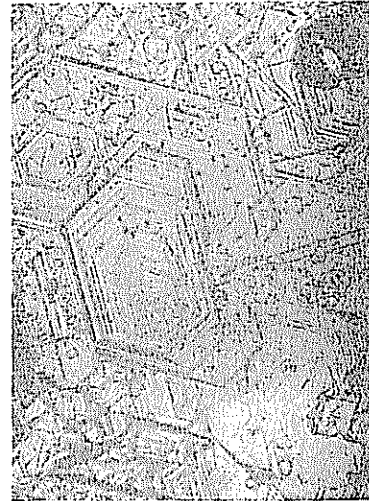


Fig. 3. Basal plane surface of purified kish showing large hexagonal stepped growth features. ( $\times$  c. 200)

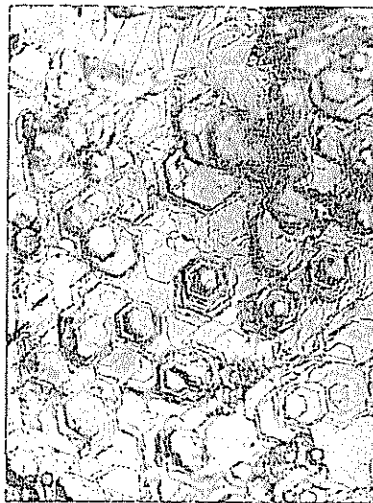


Fig. 4. Development of hexagonal pits upon air oxidation of purified kish at 850° C. ( $\times c. 200$ )



Figs. 5a and b. Coalescence of pits during a more advanced stage of air oxidation of kish purified in hydrochloric acid at 850° C. ( $\times c. 150$ )

acid (or in some cases just boiling in hydrochloric acid), followed by repeated washings in distilled water, and drying in a vacuum oven. Its structure has been further studied by transmission electron diffraction, using 50-kV electrons having a beam width of  $10\mu$ . The diffraction pattern (Fig. 1) is characteristic of a material of large crystallite size and a high degree of preferred crystallite orientation (essentially a mosaic single crystal).



Fig. 6. Roughly hexagonal holes produced by rapid attack of air at 850° C on hexagonal stepped growths of purified kish. ( $\times$  c. 200)

The basal plane (000 $l$ ) surfaces of the kish were studied by light microscopy. Typical micrographs of the unoxidized kish are shown in Figs. 2 and 3. In Fig. 2, the twin planes are readily distinguished as the striations running parallel to one another or intersecting at 60° (ref. 8). The presence of impurities on the basal plane, following treatment with hydrochloric acid only, is clearly in evidence. On a very significant portion of the surface, large hexagonal stepped growth features are in evidence (Fig. 3). It is suggested that the growth steps within these features arise from a piling-up of a large number of clockwise and counterclockwise spiral growth steps of molecular dimensions<sup>9,10</sup> (the spirals being invisible on our photographs). A substantial concentration of impurity nucleating centres from which such screw dislocations and spiral growth of graphite could occur might well be expected, considering the origin of kish.

Kish crystals were oxidized in air (1 atm.) at 850° C. Fig. 4 shows the development of a large number of hexagonal pits oriented parallel to each other and parallel to the twin lines, as previously discussed<sup>1</sup>. Figs. 5a and b show the results of coalescence of pits during a more advanced stage of oxidation. The shapes of the holes are reminiscent of those suggested by Ubbelohde, when considering defects in graphite<sup>11</sup>.

In general, it is found that the large, hexagonal stepped growths are attacked at an enhanced rate. Fig. 6 shows the result of exposure of such growths to air at 850° C for only about 5 min. Large, roughly hexagonal holes are

produced, in contrast to the relatively minor attack on other portions of the surface. However, it is not possible to decide on the basis of this result whether the presence of dislocations or the possible concentration of impurities at dislocations is of primary importance in the production of pits in the basal plane. As discussed previously<sup>2</sup>, uncertainty will remain until oxidation studies are carried out on ultra-high purity graphite of known dislocation content.

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