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Note on a Graphite-Sample with X-Ray Diagrams Free of »Orientation-effect«

S. Maričić and M. Wrischer

Institute »Ruđer Bošković«, X-Ray Laboratory and Laboratory of Electron Microscopy, Zagreb, Croatia, Yugoslavia

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We happened to obtain a sample of the residue usually collected during the decomposition of calcium cyanamide. In unpurified form it is a black-greyish mud composed primarily of calcium and carbon. By repeated purification it might finally contain up to 99.34% C, without Si, the rest (ash) being mainly iron oxide.



Fig. 1.

The investigated, purified substance is macroscopically very similar to carbon blacks, but it renders quite a definite graphite-X-ray diagram (Fig. 1). The X-ray record of a natural, good-crystallized graphite (suppl. N. Branz, Germany) was also taken for comparison under the same conditions. Ni⁺ filtered CuK α -radiation; thin-walled glass-capillary of 0.7 mm. inner diameter in a cylindrical camera of 9 cm. d., with »Ferrania«-film (Fig. 2).



Fig. 2.

It was established on microphotometering that only 100 — and 101 lines are appreciably broadened, while the widths of other hkl -lines are similar or slightly larger than the corresponding ones of the natural graphite. On the other hand, it is evident that there is no doubling of 001-lines in Fig. 1. Thus, the texture of this sample should be quite different from the plate-like form of natural graphite-particles which always produce a definite »orientation-effect«¹ (see in Fig. 2 the doubling of 002 and 004-lines).

The two graphites were also photographed by the Trüb, Täuber KM4 electron microscope using the watery suspension-drop-drying preparation technique, as well as the technique of imbedding in a nitrocellulose film.

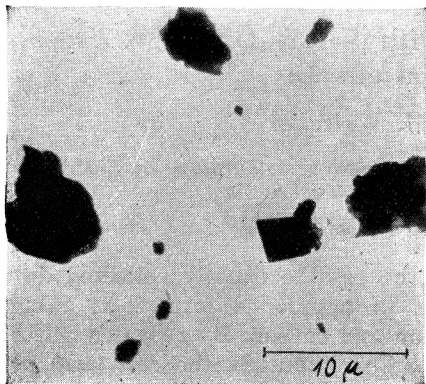


Fig. 3.

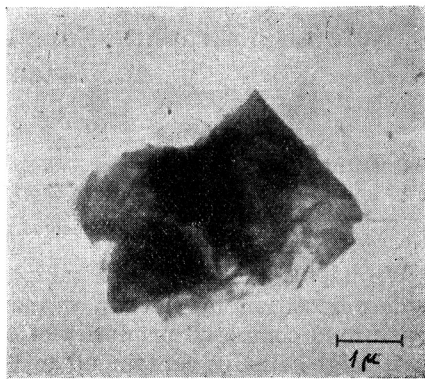


Fig. 4.

Natural graphite is composed (Figs. 3 and 4) of relatively very large plates, while the investigated sample contains highly branched aggregates built up of much smaller plate-like crystallites (Figs. 5, 6, 7). The absence of orientation-effect in X-ray records of carbon blacks is due to the sphere-like form of the particles. In our case it is caused by the loose structure of the aggregates. It was also verified that these aggregates are not held together by any

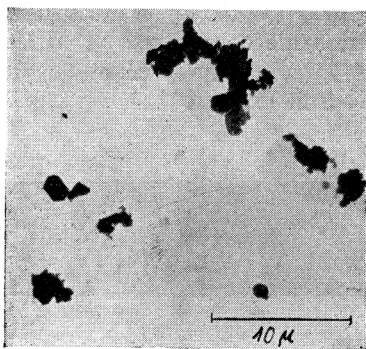


Fig. 5.

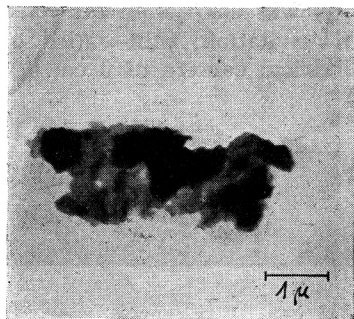


Fig. 6.

organic binder, because after a thorough extraction with benzene or amyl acetate there was no change of the texture described above.

The investigated substance is another example of graphite-formation at temperatures far below the usual graphitization-temperatures. Like »Kish«,

which is formed by decomposition of iron carbide², the present graphite is formed during the conversion of calcium carbide with nitrogen into calcium cyanamide. It is admissible to suppose that there is some direct relation between the crystal-structures of various carbides and the mechanism of graphite-formation during the carbide decomposition.

It is known that natural graphite in spite of being perfectly crystallized is useless as standard material for measurements of 001-line breadth of carbon blacks³. It seems possible that by suitable heat treatment of the described graphite, or controlled (laboratory) synthesis from calcium carbide, a good standard material (with packing-density very similar to that of carbon blacks!)

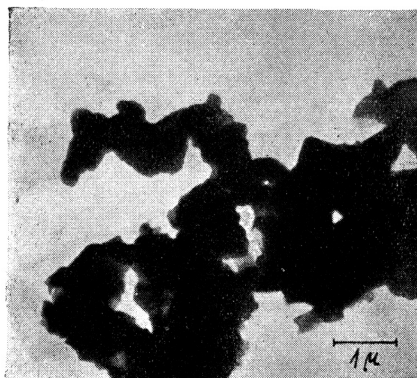


Fig. 7.

for crystallite-size measurements in carbon blacks could be obtained. The best one would be, of course, the product of carbon black-graphitization if it were not for the limitation of such a graphitization caused by the particle-sizes of carbon blacks^{2,4}.

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IZVOD**Bilješka o uzorku grafita s rentgenografskim dijagramima
bez »efekta orijentacije«***S. Maričić i M. Wrischer*

Opisan je uzorak grafita, koji kao nusprodukt nastaje pri proizvodnji kalcijeva cijanamida iz kalcijeva karbida i dušika, i koji zbog svojih sitnih pločastih kristalita povezanih u vrlo nepravilno razgranate agregate ne pokazuje na rentgenografskoj snimci inače redoviti »efekt orijentacije«, t. j. udvajanja 00l-refleksija.

INSTITUT »RUDER BOŠKOVIĆ«
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