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CATALYZED AND UNCATALYZED REACTION BETWEEN CARBON AND OXYGEN: A MOTION PICTURE STUDY

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A 16-mm. movie camera, mounted on a light microscope fitted with a hot stage, was used to observe directly the oxidation of the basal planes of natural graphite crystals in their highly purified state and with a wide number of metal impurities deliberately added.

By using a 16-mm. movie camera mounted on a Leitz Pamphot microscope fitted with a hot stage, it has been possible to observe directly the oxidation of purified natural graphite (Ticonderoga) single crystals. The motion picture shows the oxidation of four types of [000ℓ] graphite surfaces: the as-purified faces which often contain rough patches owing to sublimation and inadvertent oxidation during purification, the preoxidized faces which contain a number of hexagonal etch pits and surface steps, cleaved surfaces, and cleaved surfaces onto which have been added metallic impurities. The impurities, which were invariably added as the free metal, were introduced from an acetone suspension and were never greater than a few microns in diameter except where unavoidable aggregation had occurred. The impurities included iron, nickel, cobalt, manganese, tantalum, titanium, silver, molybdenum, and boron.

So far as the uncatalyzed reaction is concerned, this study confirms that oxidation in the <10$\bar{1}$0> directions exceeds that in the <11$\bar{2}$0> directions at temperatures up to 870°C., and nonbasal line dislocations are responsible for some of the etch pits. The film shows the unwinding of a screw dislocation, that is, oxidation along the <000ℓ> direction to give a spiral pit.

Significant differences in the behavior of various metal catalysts are readily apparent. Thus iron in the initial stages of the graphite plus oxygen reaction functions as an efficient catalyst, each particle giving rise to an etch pit. As oxidation continues, the iron particles lose their catalytic efficiency. Particles of iron no longer stimulate etch pit production. Consequently, well-defined hexagonal pits characteristic of an uncontaminated surface develop in the later stages of the oxidation. Nickel, unlike iron, retains a considerable degree of catalytic efficiency even after oxidation has continued for 105 min. at 650°C. Particles of cobalt, after their initial period of catalysis, tend to rotate on, and migrate over, the surface. This rotation and clustering process depends critically upon the nature of the ambient gas; it is pronounced in oxygen but entirely absent in carbon dioxide, both at 750°C.

Manganese and silver are extremely efficient catalysts. Pictures taken with the temperature at 720°C. in a nitrogen atmosphere show how manganese particles lead to pit production as well as to channelling of the type described previously for other metals. Titanium is also a good catalyst, but tantalum appears not to affect the oxidation in any discernible manner. Molybdenum metal first forms molten molybdenum which is a remarkable catalyst. Marked channel formation of the molten trioxide and straightening of a twin are observed. It appears likely that the exothermicity of the oxidation reaction is sufficient to relieve mechanical strain in the graphite crystal. Boron first forms molten boric oxide. Its catalytic activity is affected by the presence of water. In any case, the molten oxide decorates etch pits effectively. These studies are reported in detail by J. M. Thomas in "Chemistry and Physics of Carbon," Volume 1, pages 121–202, published by Marcel Dekker, Inc., New York, in 1966.

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