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Reaction Rates of Graphite with Ozone Measured by Etch Decoration

The problem:

To determine the reaction rates of graphite with ozone in the directions parallel and perpendicular to the layer planes. Although these reaction rates are usually measured by noting the weight loss of the samples or by measuring the gas evolved, a more precise method is required.

The solution:

The etch-decoration technique of detecting vacancies in graphite is far superior to any alternate method of studying the reaction rates of graphite with ozone. The measurements are obtained basically by counting the individual reacted carbon atoms. The etch-decoration method consists essentially of peeling single atom layers off graphite crystals without affecting the remainder of the crystal.

How it's done:

Experimentally, the method consists of puncturing the surface layer of the crystal by reaction with ozone after suitable pretreatments, then etching away the punctured layer by a more normal etchant such as O_2 or Cl_2/O_2. This removal leaves the remainder of the crystal undamaged.

For pretreatment, the graphite samples are supported on sapphire, or occasionally, on copper, polycrystalline graphite, quartz, or platinum. They are placed inside a silica tube which can be swept with purified gases, usually with helium, and preheated in these gases to temperatures as high as 900°C.

After pretreatment, the samples are preheated within the reaction furnace of an ozone line and then ejected from the pretreatment tube into the ozone furnace. After reaction with the ozone, the samples are etched in Cl_2/O_2, usually for 10 minutes at 650°C. This expands the surface vacancies in the cleavage surface to surface depressions 1000 Å wide. The circumference of these depressions is then decorated with gold at 250°C. The concentration of the resulting loops is measured in an electron microscope.

This procedure is used for reliable determination of the rates of reaction perpendicular to the layer planes of graphite, i.e., rates of primary penetration of the cleavage surface by ozone. The parallel reactions of ozone are determined by an indirect method which involves measurement of the production rate of vacancies in layer planes below the surface.

The reaction rates were found to be exceedingly sensitive to various pretreatments of the crystals, and even to the material used for supporting the crystals. The most reliable rates were obtained on crystals supported on polycrystalline graphite and pretreated at 900°C in purified helium prior to reacting with ozone. Under these conditions, the rate of the parallel reaction was 900 times faster than the rate of the perpendicular reaction. The apparent activation energies were 16.7 kcal for the faster and 20 kcal for the slower reaction.

Notes:

1. The etch-decoration technique used for determining boron in graphite is described in Tech Brief 68-10102.
2. This method has been found to succeed only for reactions of ozone and not for any other reactions with graphite, because of the abnormally low value of the anisotropy of ozone reactivity.
3. This method is only reliable on perfect crystals or crystal fragments which do not contain internal clefts or voids.

(continued overleaf)

4. Additional details and references may be found in the article: *Anisotropic Reactivities of Graphite—I. Reactions of Ozone and Graphite,* by Gerhart R. Hennig, which is published in: *Carbon*, October 1965, vol. 3, p. 107–114, Pergamon Press Ltd., Great Britain.
5. Inquiries concerning this innovation may be directed to:

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   Reference: B68-10101

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Patent status:

Inquiries about obtaining rights for commercial use of this innovation may be made to:

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