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AEC-NASA TECH BRIEF

Analytical Techniques for Determining Boron in Graphite

The problem:

To develop rapid and straightforward analytical techniques for determining the presence and mobility of boron in graphite. Because of the influence of boron on the physical and chemical properties of graphite, a highly sensitive analytical test for boron is required. The determination by spectroscopic or spectrophotometric methods is too insensitive and unreliable. These techniques are particularly unsuited for the analysis of sizable single crystals because they cannot be adequately powdered for introduction into spectroscopic electrodes.

The solution:

Two analytical techniques have been developed and tested for the determination of boron in graphite, a gold nucleation and an etch-decoration technique. The gold nucleation technique is faster, requires smaller samples, and is more precise at high concentrations than spectrographic or spectrophotometric techniques. The etch procedure, which makes it possible to locate individual boron atoms by electron microscopy, is precise at low concentrations of boron where spectroscopic techniques are unreliable. This etch technique is probably more precise than that of any chemical or radiochemical method used previously in diffusion analysis.

How it's done:

The gold nucleation method is based on the observation that lattice defects such as vacancies, or boron atoms in the cleaved surfaces of graphite crystals, under appropriate conditions will act as nucleation centers when minute amounts of gold are evaporated onto the cleavage surfaces.

The method was calibrated against a series of boronated crystals. The boronation was accomplished by induction heating at 2600°C for 3 hours in a thick-walled graphite crucible, previously impregnated several times with saturated solutions of boric acid. The boronated crystals were mixed during impregnation with powdered spectroscopic graphite, which was subsequently analyzed. It was assumed that the boron content of the crystals equaled the analyzed content of the powder. Comparison of the spectrographic analysis of the powder with the nucleation density on the crystal indicated that the nucleation efficiency of boron is only about 1%, but the technique is rapid and applicable at high concentrations where the etch-decoration technique fails.

The etch-decoration method is based on the observation that the carbon atoms surrounding a boron atom in the surface are as reactive chemically as the atoms surrounding a lattice vacancy in graphite. If cleaved crystals are gently oxidized, the enhanced reactivity at vacancies and at boron atoms causes these defects to expand into monolayer depressions in the cleavage surface. These monolayer depressions, designated as loops, can then be enhanced by gold decoration and measured in an electron microscope. This method exhibits a high degree of reproducibility and reliability, particularly at low concentrations of boron.

The etch decoration method can be used for measuring the diffusion of boron parallel to and perpendicular to the layer planes of graphite.

For measurement of parallel diffusion, batch and constant-source diffusion methods were used. In the batch method, a number of crystals were contaminated simultaneously with boron and then heated

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individually with an electron beam gun to cause diffusion of the "batch" boron. The initial impregnation was carried out at 1900°C in boronated graphite powder containing 20 ppm of boron. After impregnation, the crystals were separated from the boron source by washing in acetone or by cleaving off the outermost layer planes.

In the constant-source diffusion experiments, the boron source was a crucible machined from spectroscopic graphite filled with SPII powder or boronated lampblack. The crucible and its charge were heated in a "dirty" tube furnace long enough to give diffusion lengths of 10μ to 100μ, so that the etched loops could be clearly resolved.

The diffusion of boron perpendicular to the graphite layers was also determined by the constant-source method.

Results indicate that the mobility of boron is not very sensitive to the boron concentration for B/C values between 10^{-2} and 10^{-8}. The diffusion constants measured between 1700° and 2400°C are 6320 exp (−157,000/RT) for motion parallel to the layer planes and 7.1 exp (−153,000/RT) for motion perpendicular to the layers.

Notes:

1. The etch-decoration technique for determining reaction rates of ozone with graphite is presented in Tech Brief 68-10101.
2. Additional details are contained in *Journal of Chemical Physics*, vol. 42, no. 4, p 1167–1172, 15 February 1965.
3. Inquiries concerning this innovation may be directed to:

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Patent status:

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

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