

The Mechanism of Carbon Oxidation

Ralph T. Yang and Chor Wong
Department of Chemical Engineering
State University of New York at Buffalo
Amherst, New York 14260

Oxidation of single crystal graphite is being studied with the technique of etch-decoration and transmission electron microscopy, which was developed by Hennig et al. and Thomas et al. On the basal or (0001) plane, the carbon atoms surrounding the vacancy are the active sites, which are to be gasified and a circular pit is developed. Two sets of results have been obtained: (a) the rate of C removal per active site depends directly on the population density of the active sites; and (b) for low active-site densities, C removal continues for a prolonged period of time after O_2 is cut off from the gas phase.

Hundreds of crystals have been studied, which contained vacancies from 0.1 to 60 per μm^2 . The turnover frequency decreases with increasing vacancy density and levels off at a high density. For example, at 650°C and 0.2 atm O_2 (in Ar), the rate is 0.9 C/C/s for a vacancy density of $1/\mu m^2$; 0.6 C/C/s for $10/\mu m^2$; and levels off at about 0.5 C/C/s.

In the argon purge experiments, rates are measured during the purge after 10 min. of reaction with O_2 . The pit size is more than doubled during argon purge for surfaces with small vacancy densities, whereas no gasification occurs during argon purge with high vacancy densities.

Gasification of C on the edge sites with O_2 involves two independent processes: (a) direct collision by O_2 from gas phase (which follows the Langmuir-Hinshelwood mechanism), and (b) reaction with oxides which are chemisorbed on the basal sites and subsequently migrate to the active sites. Preliminary calculations indicate that the amount of chemisorbed oxide is 0.4 O per basal carbon for the surfaces with low vacancy densities, and that the surface diffusion coefficient is on the order of 10^{-11} cm^2/s , both at 650°C.