

The Effects of Chlorine Pretreatment on the Reactivity of Graphite in Air

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INTRODUCTION

The adsorption and interaction of halogens and halogen compounds with carbonaceous materials have been the subject of many investigations. Activated charcoal, carbon black, and coal form stable carbon-chlorine complexes on heating with gaseous chlorine, which in many cases can not be completely removed even at 1000°C (1). There have been however few studies of the effects of adsorbed halogens on the chemical reactivity of carbons, although gaseous halogens are generally regarded as inhibitors and catalyst poisons in a variety of reactions involving carbon (2,3). This paper summarizes the results of a study of the effects of pretreatment with organo-halogen compounds and also with gaseous chlorine on the kinetics of oxidation of pure graphite in air.

EXPERIMENTAL

Pure graphite powder was impregnated with a number of organo-halogen compounds and the reactivity of the treated materials towards oxygen as a function of temperature was then studied by measuring weight changes on heating in flowing air in a controlled atmosphere automatic thermobalance. In other experiments, the kinetics of oxidation of graphite in air containing the vapors of volatile halogen compounds were measured at temperatures in the range 600-900°C. The effects of pretreatment with gaseous chlorine on the subsequent oxidation behavior of graphite were also investigated and the changes induced by chlorine pretreatment on the morphology of etch pit formation on graphite single crystals during oxidation were studied using the scanning electron microscope.

RESULTS AND DISCUSSION

In general, most of the organo-halogen compounds added to graphite at room temperature subsequently desorbed on heating to 100-300°C, leaving only about 2 wt.percent or less of residual material on the graphite surface at 500°C. Strongly acidic adsorbates, such as the chloroacetic acids, rendered the graphite surface more susceptible to oxidation, probably by introducing reactive groups to the edge carbon sites of the graphite lattice. Other halogenated adsorbates inhibited oxidation of the graphite to varying degrees, the most effective additives being those with polar groups, such as -OH, -CO or -C=C-, which provided sites for attachment to the graphite surface, thereby deactivating reactive groups initially present. For example, adipoyl chloride

$\text{ClCO}(\text{CH}_2)_4\text{COCl}$, reduced oxidation rates by a factor of three in the temperature range 600-800°C, suggesting that about two thirds of the active sites on the graphite surface were blocked by halogen residues from the decomposition of this adsorbate. Hexachloroacetone $(\text{Cl}_3\text{C})_2\text{CO}$, resulted in the blocking of about half the available active sites with a reduction in oxidation rate by a factor of two.

Impregnation of graphite with volatile liquid organohalogen compounds, such as CCl_4 , CHCl_3 or C_2HCl_3 , had little detectable effect on the subsequent oxidation behavior of the graphite in air above 600°C. On the other hand, when vapors of these compounds were introduced into the air stream passing over the heated graphite samples, appreciable reductions in oxidation rates were observed. Figure 1 shows Arrhenius

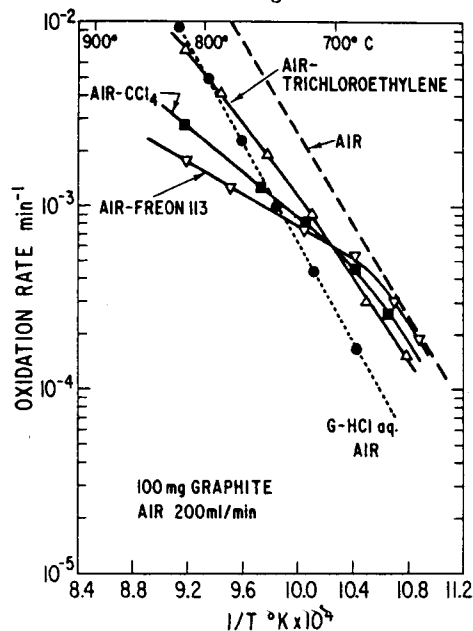


Figure 1 Oxidation rates vs. $1/T$ for graphite in flowing air and in air containing organo-halogen vapors.

plots (log oxidation rate vs. $1/T$) for pure graphite samples heated in flowing air (dashed curve) and in air saturated at 25°C with the vapors of carbon tetra-

chloride, trichloroethylene and Freon-113, Cl_2 , CF_3CClF_2 (solid curves). Although vapors of these compounds had very little effect on oxidation rates at temperatures below 700°C , at higher temperatures the inhibiting effect of the additives became increasingly marked. It seems likely that the adsorbates dissociate at elevated temperatures, forming a chemisorbed halogen residue which remains strongly bonded to the graphite surface even at temperatures exceeding 800°C . Also shown in Figure 1 is an Arrhenius curve obtained with a graphite sample which had been treated with concentrated hydrochloric acid and then evaporated to dryness before the oxidation measurements. For this treated sample, the rates of oxidation were less by a factor of four at 700°C than for pure graphite.

A series of experiments was also performed in which graphite powder was pretreated with gaseous chlorine (1% in N_2) at various temperatures prior to measuring oxidation rates in air. The effects of this pretreatment were found to be very marked when the chlorination was carried out in the temperature range 700 – 900°C . Figure 2 shows Arrhenius plots for pure graphite and for graphite samples which had been exposed to chlorine for 1 hour at 500 , 700 and 800°C before admitting air. Chlorination at 500°C had no effect on the subsequent oxidation rates, whereas treatment with chlorine at 700°C and especially at 800°C reduced the oxidation rates substantially. The magnitude of the inhibitory effect following chlorination indicated that the fractional coverage of the active surface sites by chemisorbed chlorine amounted to between 0.4 and 0.75, with maximum irreversible chemisorption occurring in the 800 – 900°C temperature range.

Pure graphite single crystals, on oxidation in flowing air at 900°C , developed regular hexagonal etch pits at dislocation cores on the basal plane surfaces. Under these conditions, pits bounded by the $\{11\bar{2}\}$ faces, oriented with sides parallel to the twin bands, were formed exclusively, as observed by other authors (4). However, following pretreatment with chlorine at 800°C , subsequent oxidation in air at 900°C resulted in the formation of unusual circular pits on the basal plane. A similar pit morphology has been observed previously (5) with graphite crystals which had been pretreated with phosphorus oxychloride POCl_3 . This interesting result suggests that chemisorbed chlorine atoms tend to remain strongly bonded at sites on the prismatic faces of the pit sides, thereby reducing the overall oxidation rate and inhibiting the growth of the hexagonal pits which propagate in the absence of halogen.

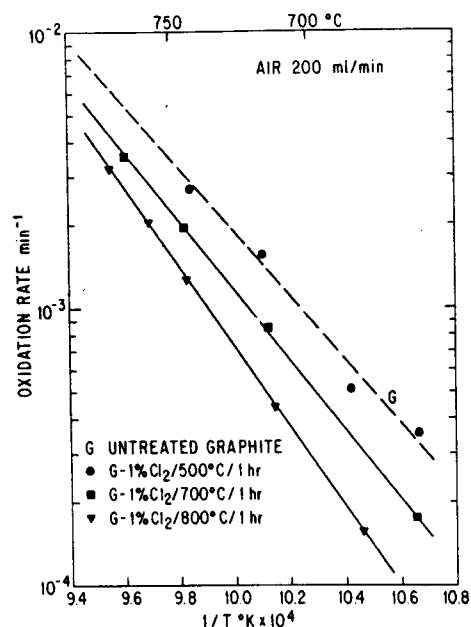


Figure 2 Effect of pretreatment with Cl_2 on oxidation rates of graphite in air. Rates vs. $1/T$ for untreated graphite and for graphite chlorinated at 500 , 700 and 800°C .

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