OXIDATION BEHAVIOR OF SOME CARBON/CARBON COMPOSITES

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The oxidation behavior of a family of commercial carbon/carbon composite materials was studied with particular attention to microstructural aspects. The composites were characterized before oxidation by X-ray diffraction and porosimetry (1); and by ignition and isothermal burnoff behavior in dry air. The major emphasis was on scanning electron micrography of oxidized samples, and some results of these studies are described here.

Four commercial laminar carbon fiber cloth/carbon binder matrix composites (Carbitex R , Carborundum Co.) were studied: C-100, carbonized fiber and matrix; C-500, graphitized fiber, carbonized matrix; C-700, C-730, graphitized fiber and matrix (different cloth weaves). The fibers were ex-rayon. A plain weave cloth was used in C-100, 500, 700 and these composites were less anisotropic than C-730, made of a flatter satin weave. X-ray diffraction showed that the composites were more graphitic, d(004) $\cong$ 3.43A (C-100), 3.39 (500), 3.36 (700,730), than the fibers, d(004) $\cong$ 3.48A (C), 3.43 (G), indicating a graphitic primary binder. Micrography revealed a laminar, oriented primary binder and a "glassy" impregnant binder phase (see Fig. 3). Bulk and immersion (benzene/tetrabromethane) densities indicated that accesible porosity (volume %) increased in the order C-500 (7.4), C-730 (8.6-9.7), C-100 (10.1), C-700 (12.3-13.5). The low C-730 porosity is due to the denser cloth weave; the high C-100 value is attributable to a deficiency of binder. Mercury porosimetry, combined with CCl_4 adsorption porosimetry and BET surface area measurements, revealed a trimodal pore distribution with mean entrance-diameters $\geq$ 100 μm (unimpregnated weave interstices, etc.); 3-8 μm (interply and yarn gaps, larger for plain weave and after graphitization); and $\sim$0.4 μm (fiber/binder and primary/impregnant binder interfaces). Some additional porosity $\leq$ 0.02 μm in C-500 was attributed to poor graphitized fiber/carbon matrix wetting and bonding. (2).

The ignition behavior (weight loss vs temperature at constant heating rate) in dry air of the composites is compared with that of some homogeneous carbon materials in Fig. 1. Oxidation resistance is poor relative to that of 2000 and 3000°C HTT glassy carbons and as-deposited and graphitized pyrolytic carbons; but it increases appreciably with graphitization for all of the materials, in agreement with other observations. Isothermal weight loss behavior in flowing dry air at 650°C is shown in Fig. 2 for the four composites. The samples were about $4 \times 6 \times 6$ mm^3 and weight loss has been normalized to unit initial external area. The small reactivity differences between C-700 and 730, and between C-100 and 500 correlate qualitatively with porosity differences; but fiber graphitization (C-500) and binder deficiency (C-100) may also contribute. The large difference between the C-100, 500 and the C-700, 730 composites results from two factors: Fall-off of unburned material may contribute to weight loss of the carbonized matrix composites; and graphitization increases purity and structural development, especially of the binder, reducing reactivity.

Sequential SEM observations on selected areas of interlaminar cleavage and polished cross section surfaces as a function of increasing 650°C burn-off revealed many details of the oxidation process. Figs. 3 and 4 illustrate some of the important features that were identified from studying a large number of micrographs. In general, the lateral surfaces of the fibers (about 8 μm initial diameter) are attacked first (even on polished cross sections), especially at the bottoms of the longitudinal grooves characteristic of ex-rayon fibers. The fiber cores remain after extensive burn off, due evidently to lower reactivity, aided by structural integrity. After the initial oxidation stages, the carbonized binder and fiber phases in C-100 are consumed at about the same rate; and the residual carbonized fiber cores are decorated with fine ash particles (Fig. 4). The average reactivity of the graphitized fibers in C-500 is lower than that of the carbonized matrix; but a strong pitting attack occurs at active sites (residual impurities or structural flaws) distributed randomly along the fiber length. The reactivity of the binder matrix is significantly reduced by graphitization in C-700, 730. Furthermore, the fiber surfaces in these composites are coated with wrinkled but oriented and adherent thin films of binder graphite. As shown in Fig. 4, these films have low reactivity and protect the fibers; oxidation attack initiates preferentially at points where the film is ruptured. Smooth oriented carbonized binder films coat the fibers in C-100, but provide less protection because they are poorly adherent and relatively reactive. The graphitized fibers in C-500 are not wet by the binder, and bare fibers are exposed on cleavage surfaces, in agreement with observations elsewhere (2).

In summary, relative apparent reactivities may be ranked as follows: laminar primary binder > glassy impregnant binder; fiber lateral surface > fiber core or binder; and for high burn off, binder $\sim$ fiber in C-100, binder > fiber in C-500, and binder < fiber in C-700,730. Oxidation resistance of these composites is improved by graphitization, despite increased open porosity. This results from reduced fiber and matrix phase reactivity (probably due to purification); and the protective effects of oriented, graphitic binder films on the fibers. The results obtained here complement those of a study of the oxidation behavior of PAN fiber/glassy carbon (PFA) matrix composites by Kimura, Shibusa, Tanaka, and Yasuda (3).

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2. Fitzer E. & Terwiesch B., Carbon 10 (4) 383 (1972)
3. Kimura S., Shibusa Y., Tanaka H., and Yasuda E., Carbon '76 Conf. Abs., Baden-Baden, June, 1976; High Temp/High Pressure, to be publ.

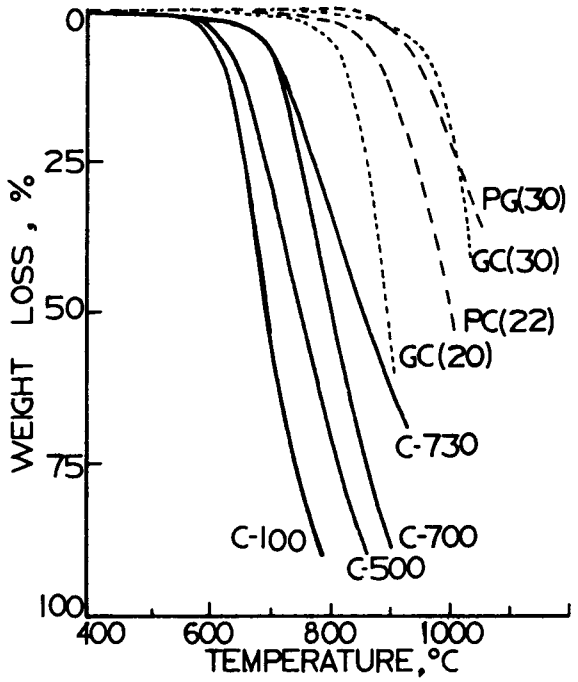


Fig. 1 Burnoff behavior at 10 C/min heating rate of the composites and some glassy and pyrolytic carbons. Numbers in brackets are HTT in 100 C.

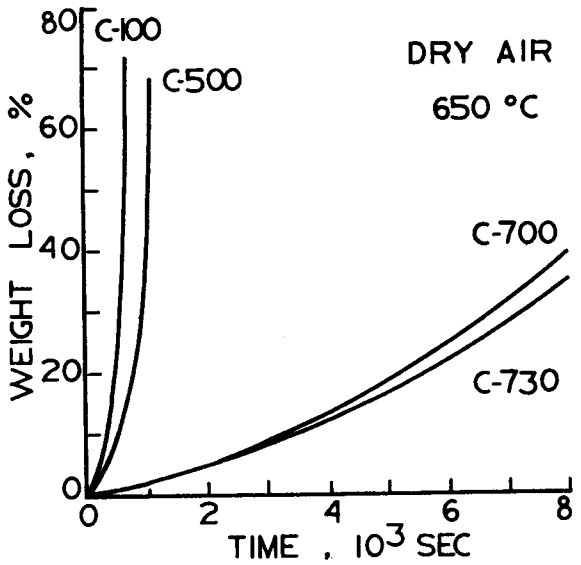
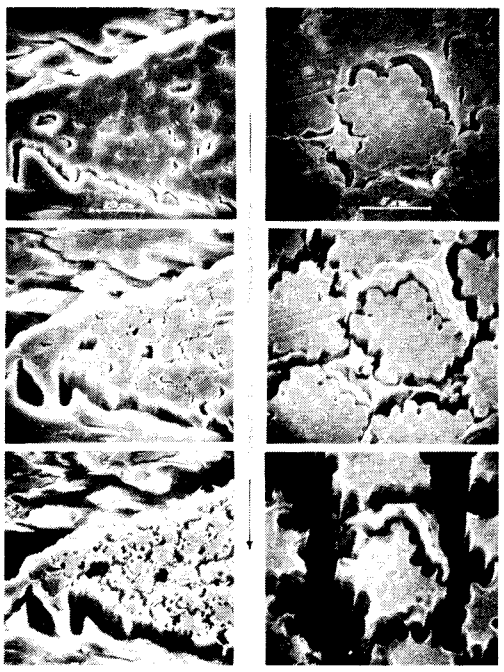
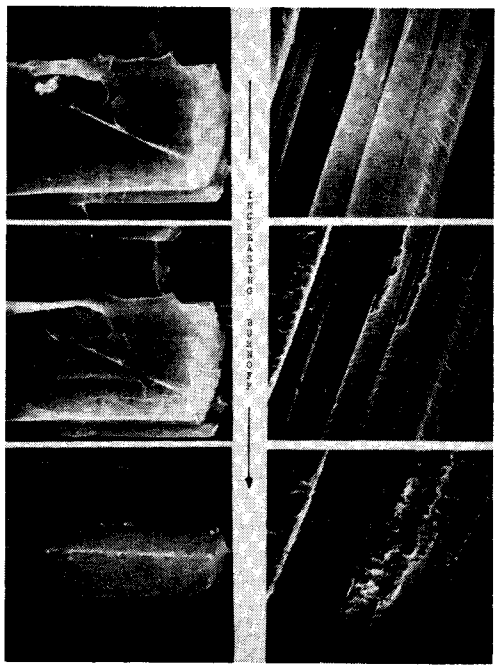


Fig. 2. Isothermal burnoff behavior of the carbon/carbon composites.



C-100 C-500

Fig. 3. Sequential SEM micrographs of selected areas of initially polished cross sections as a function of oxidation burnoff. From top to bottom, bulk sample weight loss is 0, 4, 12% for C-100; and 1, 4, 10% for C-500.



C-100 C-700

Fig. 4. Sequential SEM micrographs of individual fibers exposed on interlaminar cleavage surfaces. Bulk sample weight loss, from top to bottom, is 0, 2, 4% for C-100; and 0, 4, 8.5% for C-700.