MICROSTRUCTURAL FEATURES WHICH INFLUENCE THE ABLATION PERFORMANCE OF CARBON-CARBON COMPOSITES†

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Introduction

The response of graphitic materials to high temperature thermochemical erosion may be approached by considering the interaction of microconstituents to the environment. These microconstituents in the carbon-carbon materials examined may be generally grouped into reinforcement type, matrix form immediately adjacent to the reinforcement, matrix form in areas without reinforcement and the pore structure of the material. This paper presents key observations made on a wide variety of carbon-carbon composite post-test ablation models as a precursor to modeling efforts. By using this type of information in the modeling effort rather than a more empirical approach, the sensitivity of performance to microstructure may be examined analytically. Results may then be used to indicate directions for microstructural improvement through alternate construction and processing options.

The approach in using microstructural information for modeling thermochemical ablation response has already been demonstrated for bulk graphites [1, 2]. In these works, several different bulk graphites were characterized and relationships were found between pore structure and surface roughness which could be applied in improving thermochemical performance. Preliminary application of this approach has also been attempted—with limited success—for advanced carbon-carbon materials [3, 4]. However, the greater heterogeneity of carbon-carbon composites (as compared to bulk graphites) requires an extension of the existing approach.

Experimental Approach

In order to insure that the microstructure of the material examined was representative of that subjected to a controlled thermochemical environment, samples for observation were excised from a tested ablation model. A typical schematic of the sectioning plan for a tested ablation model is shown in Figure 1. Photomicrographs, typical of those

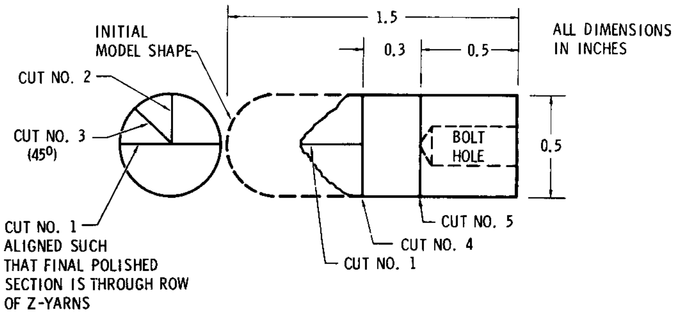

Figure 1. Ablation Model Cutting Plan

shown in Figures 2 and 3 were taken at various magnifications. The lower magnification photomicrographs were used for measuring the large features of the composite such as yarn spacing and large pore diameters. At higher magnifications, the interaction of the microconstituents of the composite with the thermochemical environment may be observed. In addition, by using polarized light microscopy (Figure 3), it was possible to determine the relative crystallographic orientation of the reinforcement and matrices.

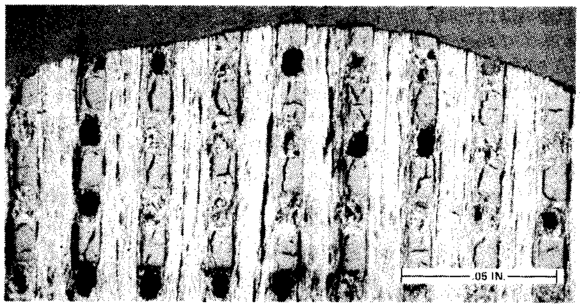

Figure 2. Ablation Model Section — Low Magnification

Additional microstructural features were measured quantitatively by using density as measured by helium displacement. Interconnecting pore size and total porosity were measured using mercury intrusion at pressures to 60,000 psi. Available internal surface area was measured using standard gas adsorption methods [5]. Finally, the availability of this internal surface area was measured using a gas permeability test.

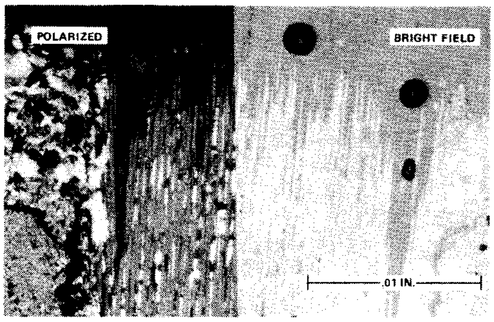

Figure 3. Section of a Yarn Normal to Ablating Surface

From these tests a description of the total pore structure, shown in Figure 4, was obtained. This information can now be related to composite fabrication details for establishing relationships between processing and microstructure and, for exploring relationships between thermochemical erosion mechanisms and material microstructural features.

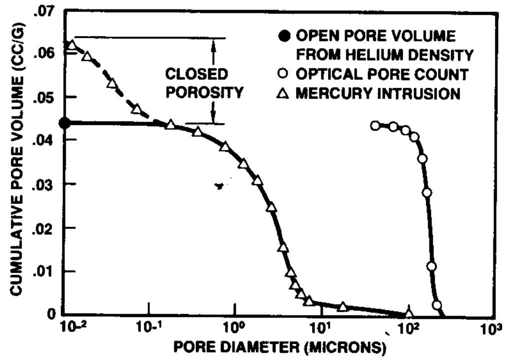

Figure 4. Pore Charaterization of a 3D Carbon-Carbon

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Carbon-Carbon Composite Variables

Eleven different carbon-carbon composite types are being characterized on this program. The reinforcement types used in the various composites include Thornel 50, HMS Pan, Thornel 300 and Union Carbide's pitch precursor yarn. Constructions using 3D orthogonal geometry and fine weave pierced fabric geometries are being evaluated. Weave spacing variations in the class of 3D orthogonal materials are also being evaluated.

Most of the materials have been subjected to processing with coal tar pitch at 15,000 psi. A major variable in processing, however, is whether or not CVD was used prior to the 15,000 psi densification. Several composites utilizing lower pressures and/or combinations of both low and high pressure processing are also included. Table 1 is a list showing the variables involved for all composites being characterized on the program.

TABLE 1 COMPOSITE VARIABLES

REINFORECEMENT TYPE:	MATRIX PRECURSORS:	PROCESSING VARIABLES:	MATRIX COMBINATIONS:
		PRESSURE:	
THORNEL 50	COAL TAR PITCH		— EPOXY/PHENOLIC + PITCH
THORNEL 300	PETROLEUM PITCH	— 1000 PSI	— CVD + PITCH
HMS 1000/3000	EPOXY/PHENOLIC	— 5000 PSI	— LOW + HIGH PRESSURE
VSA (PITCH)	CVD CARBON	—10000 PSI	
		—15000 PSI	

Discussion

In considering the effect of microstructure on the thermochemical ablation performance of carbon-carbon composites, it is convenient to divide the material into two zones. The first zone concerns the surface of the material at the material-thermochemical environment interface. The second zone is that material immediately beneath the surface which, if available to enter into the reaction, is preconditioned and will, at some later time affect the interface between the material and the environment.

The relative rates of thermochemical erosion of the composite constituents at the specimen surface can be readily observed on photomicrographs. These constituents consist of the yarns normal surface (or nearly so), yarns transverse to the surface and pockets in the reinforcement structure filled with matrix material. Differential rates of erosion of the constituents lead to a roughened surface which interacts with the ablation environment and results in enhanced heat transfer.

In some environments, the boundary layer is relatively insensitive to the behavior of the large, isolated discontinuities and is primarily dependent on the roughness developed within the individual constituents to provide numerous roughness elements. The most significant consideration in this regard is the axial yarn bundles which have differential erosion rates between the filaments oriented normal to the surface of the specimen and the matrix material between these filaments. The type, orientation and density of this matrix material affects its performance. In addition, differential thermal expansion between the filament and the matrices may lead to an open interface which is readily attacked. Roughness developing in this manner can then induce turbulent flow and thus enhance heat transfer rates.

The response of a graphitic material in-depth is dependent on the internal surface available for reacting with the thermochemical environment. This is controlled by both the permeability of the material and the surface associated with the pore structure. Also, the primary thermochemical erosion mechanism (i.e. either sublimation or oxidation/reduction reactions) are important. If an extensive amount of internal surface is available then a significant portion of the mass loss of the material may be from below the surface. This material is then preconditioned and may affect the total mass loss in two ways. First, existing discontinuities in the material may become enlarged and, when they reach the surface, will result in higher surface roughness. This higher roughness, in turn, interacts with the environment to produce higher heat transfer rates and therefore higher total mass loss for the same external conditions. The other effect, which is more important in bulk graphites than in carbon-carbon composites, is that the internal material may be pre-weakened and upon, reaching the surface, may fail mechanically. A photomicrograph showing fairly extensive in-depth erosion is presented in Figure 5.

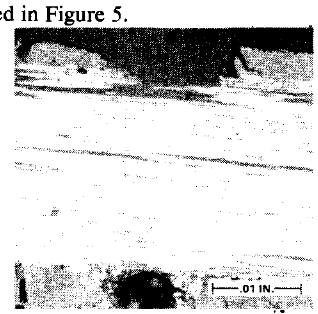

Figure 5. In-Depth Material Erosion at an Ablating Surface

By having the sensitivity of permeability and surface area defined by a model which quantitatively predicts performance in a given environment, it is then possible to make material improvements through process alterations and subsequent microstructure alterations thus tailoring the material for a special environment.

Summary

Microstructural characterization is being conducted on a number of carbon-carbon composites to provide information for use in quantitative models to predict performance in a thermochemical ablation environment. Heat transfer considerations as influenced by the roughness of the material in the environment may be used by including measured geometric discontinuities as determined using photomicrographs. The role of reactions occurring below the surface may also be considered by including measured permeability and specific internal surface area in the modeling effort. The developed model can then be used to show the sensitivity of various microstructural elements to performance and direction may be given for fabrication changes leading to materials with enhanced performance.

References

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