PERMEABILITY, POROSIMETRY, AND MICROSTRUCTURE OF 3D CARBON-CARBON COMPOSITES

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Making low-porosity carbon-carbon composites, reinforced with graphite fibers in three orthogonal directions (3D weave), includes repeated impregnations (with pitch, resin and/or CVD), pyrolyses, and graphitizations [1][2][3]. The microstructure of composites containing Thornel-50 yarns, graphitized to about 2700°C, includes cracks between yarn bundles forming a continuous network, shown schematically in Figure 1 [4]. These cracks are believed to result from thermal stresses induced by the anisotropic contractions of yarn bundles during cooling from the peak graphitization temperature [4]. The width of the cracks is a partial measure of the creep extension of the yarn bundles during heating to the peak graphitization temperature. This view of microcrack formation is supported by high yarn-bundle stresses estimated to occur during the graphitization cycle [5], and by photomicrographs of 3D composites before and after graphitization [6].

A consequence of the postulated mechanism of crack formation is the closure of the cracks upon reheating the composite. Observations of samples heated to 1600°C in a scanning electron microscope corroborate this prediction and show reheating such composites to the graphitization temperature can reduce porosity to less than half the value measured at room temperature [7]. That is, the cracks at room temperature account for more than half the void volume of low-porosity composites.

Consideration of the crack network, as it appears at room temperature, suggests:

a) the cracks are the major path contributing to permeability of these materials to fluids,
b) the cracks are the main passages by which mercury penetrates the pores of the composite in porosimetry tests, and
c) a relation should therefore exist between gas permeability and the equivalent pore entrance size inferred from mercury porosimetry.

Experiments

The composites described by Seibold [3], and one other, were studied. Variations in the densification and graphitization process details produced samples exhibiting a range of permeability and porosimetry data (Table 1).

Permeability was measured at room temperature by passing nitrogen through disks 0.8 cm thick. The disk axis was parallel to one set of yarns. Pressures up to 20 atmospheres were applied to one face of the disk in a gasketed fixture while the other face was maintained at one atm. Both the viscous and inertial permeability coefficients (α and β, respectively) were estimated by fitting to the data the equation of Green and Duwez [8]:

$$\frac{p_i^2 - p_o^2}{(2\mu RTL)\dot{m}} = \alpha + \beta\left(\frac{\dot{m}}{\mu}\right)$$

where R, μ, T are the gas constant, viscosity, and temperature, L is the disk thickness, $\dot{m}$ is the mass flow of gas, and p_i and p_o are the inlet and outlet gas pressures.

Mercury intrusion tests were conducted by standard means. Some of the results are shown in Figure 2. The point of steepest rise in the curve of penetration vs. pressure was taken as the measure of the most representative pore-entrance size. This modal value of the equivalent pore diameter ranged between 5 and 20 microns. The typical crack widths observed on photomicrographs are also in this range.

Figure 3 shows the empirical trend between permeability (as represented inversely by the viscous coefficient) and modal equivalent pore size. It may be noted that attempts to relate permeability to bulk density, open porosity, or internal surface area (by BET) did not show as good a trend.

Table 1

Material *	Viscous Permeability Coefficient 10^{12} per m^2	Inertial Permeability Coefficient 10^{9} per m	Modal Equivalent Pore Dia. μm
D	24	1.0	10
A	59	1.9	6
DD	10	0.05	11
R	19	0.8	12
RR	110	5.0	5
B	11	0.4	15
C	190	4.4	5
DM	3	0.04	18
BB1	31	1.6	9
BB2	9	0.3	9
BB3	30	1.2	10
BC1	8	0.2	18
BC2	9	0.2	10
BC3	9	0.2	13
GE223*	30	0.5	9

*All materials used Thornel-50 yarn in a "223" weave; spacing of parallel yarn bundles was about 0.8 mm. GE223 (core of Billet 331) was processed with CVD plus five pitch cycles (1000 atm pyrolyses) and 2700°C graphitizations. Other materials had pyrolyses at 68 atm; for their descriptions see Seibold [3].

Conclusions

The reasonably good correlation of Figure 3, between permeability and porosimetry data, and the similarity of microscopically-observed crack widths to the modal pore sizes inferred from porosimetry, offer indirect support to two commonsense notions:

a) the observed crack network is the major pathway for both viscous gas flow and capillary liquid penetration into 3D carbon-carbon composites
b) the permeability of the composite will depend to a large extent on the width of the cracks.

Closure of the cracks upon heating the composite may therefore be expected to drastically reduce the permeability at temperatures near the graphitization temperature. Development of methods to measure permeability at elevated temperatures should be encouraged as some applications of 3D carbon-carbons (e.g. rocket nozzle liners and reentry-vehicle nosetips) involve exposure to hot high-pressure gas.

The data presented suggest there may be a basis for estimating the permeability of similar composites from porosimetry and/or microscopy, when permeability data is lacking. It should be noted that all the composites studied here were of the same weave and yarn; other weaves may give quantitatively different trends, although the same qualitative relationships are expected.

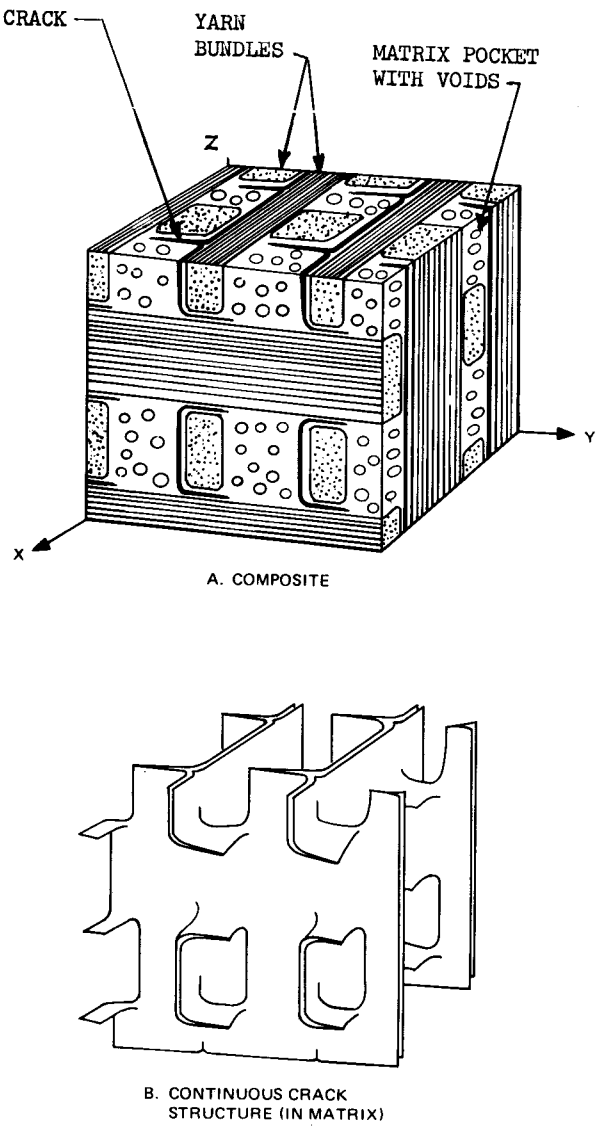

Figure 1. Microstructural Features.

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Acknowledgement

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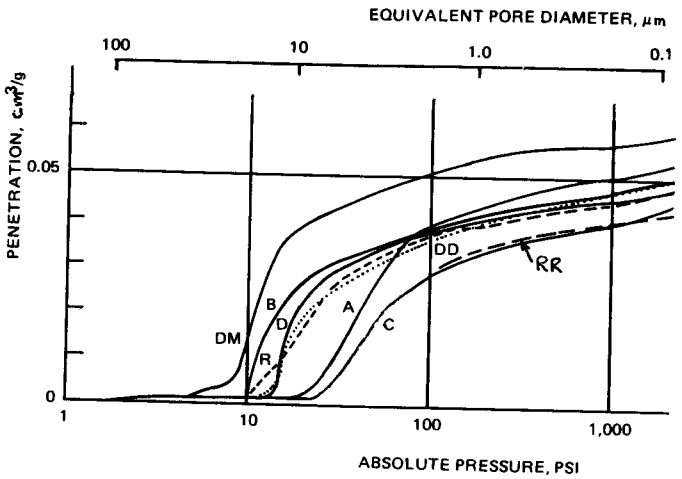

Figure 2. Representative Porosimetry Data.

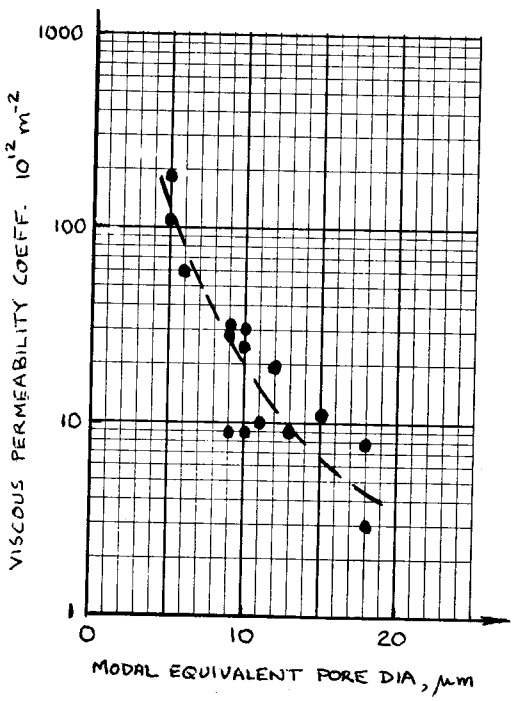

Figure 3. Trend of Data.