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Achieving high density of 3D carbon-carbon composites requires repeated impregnations of the weave (with pitch, resin, and/or pyrolytic carbon), pyrolyses, and graphitizations [1][2][3]. The bulk density of graphitized 3D composites is limited by the opening of cracks on cooling from the graphitization temperature [4], the "freezing-in" of pyrolysis-gas bubbles in pitch-precursor carbon, and the formation of voids or cracks as the solidified matrix shrinks during pyrolysis and graphitization. Thus, even if the apparent density of the matrix and fibers were to be that of perfect graphite (about 2.26 g/cm<sup>3</sup>), the attainable bulk density of the composite would be measurably lower. The bulk density of near-isotropic polycrystalline graphites is similarly limited to about 2.1 g/cm<sup>3</sup> [5][6]. Another limitation is the dimensional growth of carbon-carbon billets, in the later stages of processing, which sometimes results in reduced density in spite of mass gains [1].

Crack Volume

The volume of crack space V<sub>C</sub> formed in a unit volume of composite on cooldown to room temperature T<sub>R</sub> from the crack-opening temperature T<sub>C</sub> may be estimated:  $\frac{V_C}{V_C - T_R} = 2\alpha_{Yt}[1 - \xi(1 - \xi)] + 3\alpha_M \xi(1 - \xi) - \alpha_{Ya}[2 + \xi(1 - \xi)]$  (1) where the  $\alpha$ 's are the thermal expansion coefficients of the yarn bundles ( $\alpha_{Yt}$  is transverse and  $\alpha_{Ya}$  is parallel to the axis of the fibers) and the matrix ( $\alpha_M$ ), and  $\xi$  is the ratio of x<sub>z</sub> to x (Figure 1) for weaves in which x = y and x<sub>z</sub> = y<sub>z</sub>. Equation (1) assumes cracks, of the type sketched in Figure 1, completely relieve the internal tensile stresses that would act during cooldown as a result of  $\alpha_{Yt} > \alpha_M > \alpha_{Ya}$ .

Calculations made using equation (1) imply three to five percent of the volume is occupied by the crack space. Representative values for thermal expansivities were used: yarn-bundle expansivities ( $\alpha_{Yt} = 7$  to  $13 \times 10^{-6}/^\circ\text{C}$ ,  $\alpha_{Ya} = 1$  to  $1.8 \times 10^{-6}/^\circ\text{C}$ ) were based on data for unidirectional carbon-carbons made with high-modulus fibers [7][8] and on in-situ measurements using elevated-temperature microscopy of 3D composites [9];  $\alpha_M$  was taken as  $5 \times 10^{-6}/^\circ\text{C}$ , equal approximately to that of ATJS graphite. The crack-opening temperature was taken as ranging from about 2000°C to 2800°C [9]. Sensitivity of crack volume to weave geometry, as represented by  $\xi$ , appears to be a second-order effect.

Pore Size

3D carbon-carbons, densified with pitch at pyrolysis pressures p below a threshold value p\*, tend to contain one pore in each matrix pocket. The threshold pressure may be viewed as the pressure at which the pyrolysis gas occupies the same volume as is made available by the shrinking liquid pitch; that is, at p\* there is no need for liquid pitch to be ejected from the composite during the initial stages of pyrolysis. At p < p\*, outflow of pitch promotes coalescence of gas into one large bubble in each matrix pocket. Composites pyrolyzed at (or above?) p\* will tend to retain a number of separate small pores in each matrix pocket. Judging

from microstructural views of finished composites[10], p\* is in the vicinity of 900 atmospheres; probably p\* is quite sensitive to the grade of pitch and to the thermal and barometric histories of the pyrolysis.

These speculations lead to the concept of a "mechanical" carbon-yield factor Y' (which is pressure dependent) in addition to the coke-yield factor Y (which appears insensitive to pressure above about 50 atm [2][11]). Thus, the volume fraction c of graphite (of apparent density  $\rho_G$ ) retained within a matrix pocket after impregnation with a unit volume of liquid pitch (having an initial density  $\rho_T$ ) is:

$$c = Y Y' \rho_T / \rho_G \quad (2)$$

Values of Y' above one might occur at p > p\*.

The bulk density of the 3D carbon-carbon may be given as:

$$\rho_B = \rho_{AY}(V_Y - V_{YP}) + \rho_{AM}(V_M - V_P) \quad (3)$$

where the volume fractions add up to unity:

$$V_Y + V_M + V_{YP} + V_P + V_C = 1 \quad (4)$$

and  $\rho_{AY}$  = apparent density of yarn bundle  
 $\rho_{AM}$  = " " " matrix in pockets  
 $V_Y$  = volume fraction of yarn bundles  
 $V_M$  = " " " matrix pocket  
 $V_P$  = " " " matrix-pocket pores  
 $V_{YP}$  = " " " yarn bundle voids  
 $V_C$  = " " " crack space

For illustrative purposes, we assume a balanced weave (x = y = z, x<sub>z</sub> = y<sub>z</sub> = z<sub>m</sub> = 0.5x, v<sub>m</sub> = 0.5, see Fig. 1). If N pores of dimension x<sub>p</sub> reside in each matrix pocket:

$$V_P \cong N \left( \frac{x_p}{x_m} \right)^3 V_M \quad (5)$$

Combining equations (3), (4) and (5), one can derive the relations between average pore size and bulk density shown in Figure 2. Additional assumptions behind Figure 2 are  $\rho_{AY} = \rho_{AM}$ , V<sub>C</sub> = 0.04, and that V<sub>YP</sub> is either zero or included in V<sub>C</sub>. The assumption implicit in this treatment, that the yarn bundles are essentially fully densified and do not gain in density while the matrix pores are diminished during the last several process cycles, receives support from process histories of unidirectional and 3D composites densified in the same batch [12].

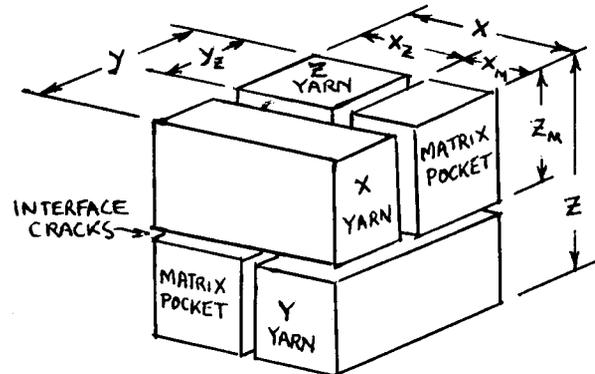


Figure 1. Sketch of Cracked Unit Cell

Billet Growth

Each additional impregnation/pyrolysis/graphitization cycle contributes to the fractional mass gain and the fractional volume growth of the billet:

$$\frac{\Delta m}{m} = \frac{\rho_A}{\rho_B} [C_c V_c + C_p V_p] \quad (6)$$

$$\frac{\Delta V}{V} \approx \frac{4}{3} C_c G V_c \quad (\text{for balanced weaves}) \quad (7)$$

where  $C_c$  = volumetric yield of graphite in cracks  
 $C_p$  = " " " " " in pockets  
 $G$  = factor to account for other effects on the creep strain of yarn bundles during graphitization  
 $\rho_A$  = apparent density of the composite

A decrease in bulk density can occur with added processing if the fractional volume growth exceeds the fractional mass gain. Combining equations (3),(4),(5) (6) and (7), gives the following estimate for the maximum attainable bulk density  $\rho_B^*$ :

$$\frac{\rho_B^*}{\rho_A} = \frac{C_p + V_c (C_c - C_p)}{\frac{4}{3} C_c G V_c + C_p} \quad (8)$$

The volumetric yields may be estimated from equation (2) using reasonable estimates of the various factors:  $Y$  = about 0.8 [2];  $Y' = 1.0$  for the crack space and for pores densified at  $p > p^*$ , and  $Y' =$  about 0.3 for pores densified at  $p < p^*$ ;  $\rho_I/\rho_G = 0.67$  [13]. Based on these preliminary estimates, and taking the creep factor  $G$  as unity, maximum density is predicted to range between  $0.92 \rho_A$  and  $0.95 \rho_A$ , for an assumed crack volume  $V_c = 0.04$ . The growth limits to bulk density are schematically shown in Figure 3.

Concluding Remarks

The bulk density of graphitized 3D carbon-carbons appears limited to about 92 to 95 percent of the apparent density of the constituents. Principal factors contributing to this limitation are the crack space that forms during graphitization and the billet growth phenomenon. The variation of pore size with bulk density is greatest as the maximum bulk density is approached; at high bulk densities, pore size is also quite sensitive to variations in apparent density. In composites densified with pitch, pore-size sensitivity will be reduced if pressures higher than a threshold value are applied during pyrolysis while the pitch is still fluid.

These conclusions are derived from the simplified illustrative calculations offered above. The issues deserve more detailed treatments as to the influences of weave geometry, yarn-bundle porosity, and differences between the apparent densities of the yarn bundles and the matrix pockets, among other factors. Study of the process parameters that control apparent density and the in-situ volumetric yields of graphite appears worthwhile, as does study of the creep behavior of yarn bundles at high temperatures.

Acknowledgement

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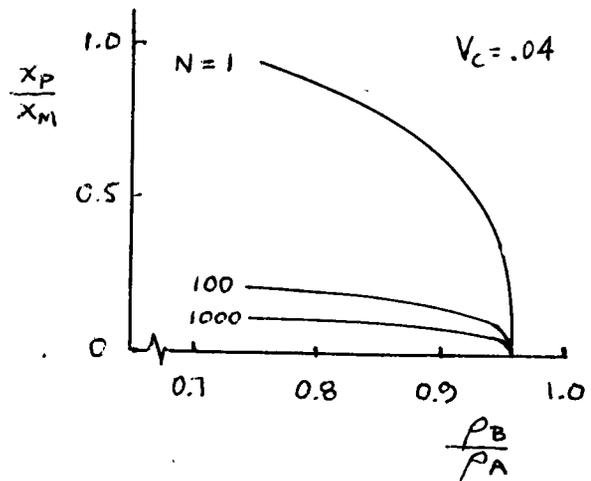


Figure 2. Pore Size vs. Density (No Growth)

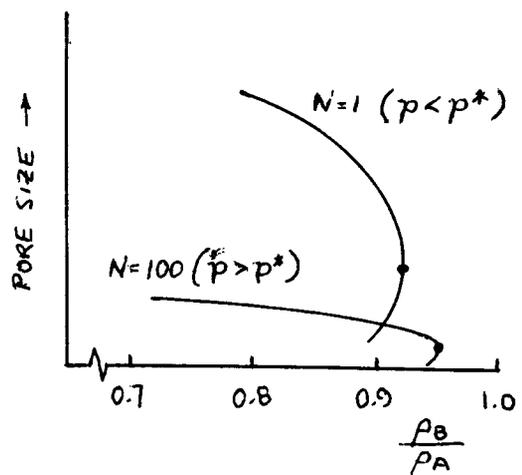


Figure 3. Growth Limits to Density (Schematic)