DENSIFICATION OF CARBON-CARBON COMPOSITES AT 30 KSI

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Introduction

The high-pressure-impregnation-carbonization (HPIC) cycle, developed at Y-12, was designed to densify carbon-carbon composites by impregnating with pitch and carbonizing at ∿ 100 MPa in a hot-gas autoclave. The 100 MPa pressure was utilized since this was the maximum operating pressure of the existing vessel. Considerable discussion has developed as to the effect of pressure during impregnation and carbonization. Comparison of densification at 100 MPa with low-pressure impregnation (3 MPa) and atmospheric pressure carbonization indicated a doubling of the coking yield. A corresponding decrease in the number of cycles needed to obtain the desired composite density was observed.

A hot-gas autoclave with capabilities to 200 MPa at 650°C has recently been made operational at Y-12. This new vessel is designed to evaluate the effects of pressure on the densification of carbon-carbon composites.

The first stage in this investigation was to provide a direct comparison of identical billets processed at 100 and 200 MPa. Porous carbon billets were employed to determine project feasibility before more expensive 3-D woven billets were processed.

Presentation of Experimental Work

The HPIC cycle has been used to densify woven, 3-D carbon-carbon composites for several years. The standard cycle (shown in Figure 1) uses a pressure of ∿ 100 MPa for impregnation and carbonization purposes. There has been much discussion as to the necessity of using 100 MPa in this cycle. Low-pressure impregnation (∿ 3 MPa) with carbonization at atmospheric pressure will yield a part of approximately the same final density but will require 2-3 times the number of cycles. The effect of using higher pressures has not yet been analyzed.

The initial stage of this project was to investigate the effects of 200 MPa impregnation and carbonization on the densification of carbon-carbon composites. The first stage was to use porous carbon as the sample material to approximate the amount of porosity of woven billets. Six porous carbon billets (130 mm dia. x 180 mm long) were procured with small pieces of stock to serve as samples. All six billets were labeled, indexed, measured, and weighed before being heat treated to ∿ 2900°C. This step assured that all billets had been heated to a temperature higher than the highest temperature to be used in the densification process. The bulk densities measured after this heat treatment ranged from 1.13 to 1.26 gm/cm^3. For the first comparison test with 15-V pitch, two billets which had approximately the same bulk density were chosen. One billet (HP-5) was to be densified using the standard HPIC cycle (Figure 1) and the other (HP-2) using the ultra-high-pressure impregnation and carbonization (UPIC) cycle (Figure 2). The UPIC cycle closely approximates the HPIC cycle except that the pressure was doubled.

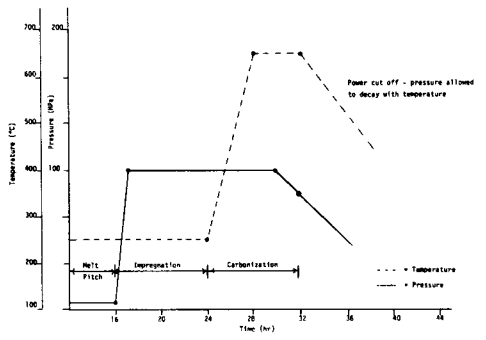

Figure 1. HPIC CYCLE.

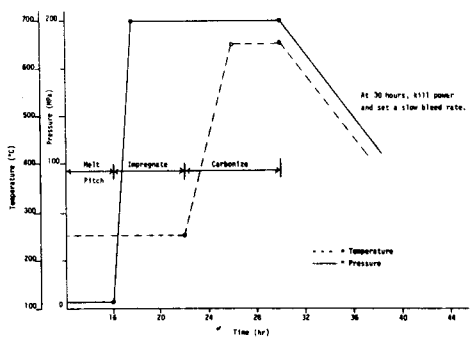

Figure 2. UPIC CYCLE.

The graphitization cycle was the standard cycle used for nose-tip preforms (Figure 3). Although there is reason to believe the porous carbon billets would not survive several of these graphitization cycles, this cycle was employed for comparison purposes.

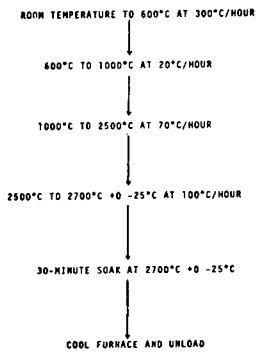

Figure 3. HEAT-TREATMENT CYCLE, TOTAL TIME—46 HOURS.

Note: Furnace atmosphere is argon flowing at rate of 1.0 scfm.

For the initial phase of the program, two impregnants were used—Allied Chemical's CP-277-15V (coal tar pitch) and Ashland's A-240 (petroleum base pitch). The base-line impregnant for the Air Force nose-tip densification program is 15-V pitch. The A-240 pitch has a higher sulfur content and a lower coking yield. The billets were to be densified with each pitch in each type of cycle.

The data derived from measurements of the billets are given in Table 1. It should be noted that the coke yield in the can was approximately the same for both the HPIC and UPIC cycles for the same type of pitch. The A-240 coke yield was ∿ 6 wt % less than that of 15-V. From these data, the UPIC cycle gave a slightly higher weight gain than the HPIC cycle. The slight compaction of the billet in the UPIC cycle, which is alleviated in the graphitization cycle, is not apparent from Table 1.

Table 1

Physical Measurement Data for the Densification of Porous Carbon

Billet	After Original Graphitization	After 1st Cycle Densification	Percent Changes	After 2nd Cycle Densification	Percent Changes
HP-2					
15-V Pitch - Vol (cc)	2124.370	2123.496	-0.041	2135.195	+0.51
UPIC Cycle - Wt (g)	2604.361	3488.389	+33.9	4002.966	+53.70
Density (g/cc)	1.226	1.643	+34.0	1.875	+52.94
HP-5					
15-V Pitch - Vol (cc)	2132.603	2138.392	+0.281	2149.774	+0.81
HPIC Cycle - Wt (g)	2705.171	3474.053	+28.4	3850.176	+46.02
Density (g/cc)	1.269	1.625	+28.1	1.837	+44.76
HP-3					
A-240 Pitch - Vol (cc)	2129.960	2129.281	-0.03	2145.133	+0.71
UPIC Cycle - Wt (g)	2508.096	3316.552	+32.23	3837.832	+53.0
Density (g/cc)	1.178	1.558	+32.26	1.788	+51.9
HP-6					
A-240 Pitch - Vol (cc)	2118.487	2117.872	-0.03	2130.413	+0.56
HPIC Cycle - Wt (g)	2492.007	3197.573	+28.31	3674.795	+47.46
Density (g/cc)	1.176	1.510	+28.40	1.725	+46.68

Note: All percentages are based on original graphitization.

As shown in Figures 4 and 5, carbonization at 200 MPa appears to inhibit mesophase coalescence. This phenomena has been observed on both porous carbon and very fine porosity chopped fiber materials using Allied 15-V pitch as the impregnant. However, uncoalesced mesophase spheroids were not observed in the porous carbon billets after the second UPIC cycle using 15-V pitch and in any runs using Ashland A-240 pitch. Experiments will be reported which were done at 200 MPa with four identical porous carbon billets

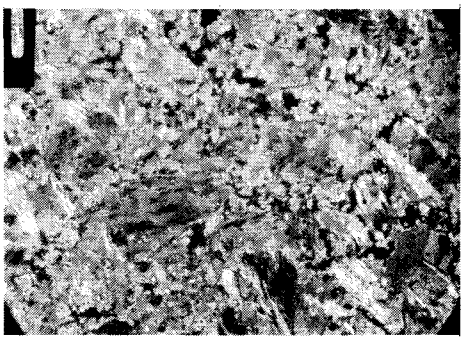

Figure 4. HP-2 AFTER FIRST CYCLE UPIC.

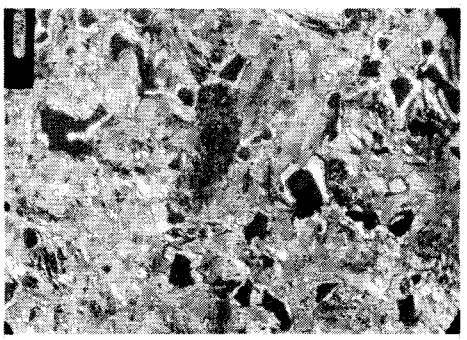

Figure 5. HP-5 AFTER FIRST CYCLE HPIC.

with four different pitch types; A-240, Allied 15-V, 30M and Koppers pitch made to 15-V specification. This approach will determine the reproducibility of this phenomena and its dependence on pitch properties.

The effects of the 200 MPa process on densification of typical woven three-dimensional orthogonal (3-D) composites will also be reported. The program includes densification of several 3-D billets and comparison of the microstructure obtained in each cycle with matching billets processed in the standard 100 MPa process. The effect of significantly increased pore size of the 3-D billets as compared to the porous carbon billets will therefore be determined. This will provide the first real microstructural examination of sequential densification of carbon-carbon composites at these pressures.

The development of small spheroids in the normally large porosity offers an attractive option for tailoring the composite microstructure. The current densification process attempts to fill the pore from the pore wall inward with sequential deposits. This process results in a distribution of partially filled large pores. Inhibiting mesophase coalescence to retain spheroids which break up the large porosity into a number of small pores would provide not only improved densification possibilities resulting in higher densities with fewer cycles but also improved ablation performance. As ablation is controlled by porosity size and distribution rather than density per se, the fine evenly distributed porosity demonstrated in the 200 MPa results may significantly improve performance, particularly transition behavior, in aerospace applications. The fact that the second cycle microstructure does not show this behavior may indicate a process composed of decreasing pressures with subsequent cycles. A process of this type could optimize performance, densification, and cycle cost.