RECENT ADVANCES IN RAPID VAPOR-PHASE DENSIFICATION OF THICK REFRACTORY CARBON-CARBON COMPOSITES

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Refractory carbon fiber-matrix composites are attractive for use in aircraft brake pads and in uncooled engine and rocket sections due to their low density and superb mechanical and thermal properties. Most articles are produced by densification of porous, final-shape fiber preforms, by means of multiple cycles of isothermal isobaric chemical vapor infiltration (IICVI) and/or liquid resin impregnation with high-temperature treatment. In CVI, a precursor gas (e.g., CH_4) flows over and around preforms held at a temperature sufficient to decompose the gas and deposit the desired solid C matrix within the pores, thus increasing the density of the preforms. CVI produces high-purity matrices and near-net-shape composites at lower pressures, $p = 10^{-3}$-10^{3} Torr and temperatures, $T = 600$-$1500^{o}C$ than other methods; the deposition rate increases as $p^{n}\exp(-\Delta H/kT)$. In IICVI, a few hundred preforms may be densified simultaneously in a hot-wall reactor, for 600-2000 h. Because the surface pores of the preforms become clogged before the desired density is reached, infiltration has to be interrupted repeatedly to grind the external surfaces. IICVI also produces lower density in the interior regions of the articles and suffers from low precursor conversion efficiency (1-3%). Increasing the temperature or pressure to reduce the densification time in IICVI may result in unwanted gas-phase powder nucleation, earlier surface crusting and poor-quality matrix microstructure. Different published routes to reduce the densification time are summarized in Table 1 and Fig.1 and described in greater detail in Ref.1.

A novel, patented[2], single-cycle method, inductively-heated, thermal-gradient, isobaric CVI was recently demonstrated to simultaneously densify three 10.8 cm o.d. x 4.4 cm i.d. x 3.0 cm thick non-woven PAN-based C preforms in 26 h. The disks were placed around a Mo or Al_2O_3 mandrel, spaced $\approx$1 cm apart, the assembly was located inside a 15 cm i.d. x 22 cm long, water-cooled copper induction coil in a water-cooled vacuum chamber and exposed to flowing cyclopentane (C_5H_{10}) vapor. An electrically conductive mandrel was unnecessary, as the electrical conductivity of these preforms was sufficient to enable their direct Joule heating by circumferential induced currents flowing inside them; this resulted in an inside-out thermal gradient and produced temperatures of almost 1200°C inside the disks[3], higher by $\approx$200°C than in IICVI. The temperature profile in the disks was dominated by the radiation losses, Q, from their surfaces staring at the water-cooled walls, $Q[W/m^2] = 5.67\times10^{-8}\varepsilon(T^4_{od} - T^4_{wall})$. Axial heat losses were reduced with grafoil plates placed above and below the mandrel; in some runs, a quartz tube was inserted as a flow channeler between the preforms and the coil. The parameters of the induction power supply (8.8-13.2 kW, 4.9-8.6 kHz), pressure (20-100 Torr) and flow rate (170-540 sccm) were controlled. Very high average carbon pick-up rates per disk, 9.5 g/h or 10.6%/h, were obtained (Fig.2). Whole-disk densities were increased from 0.4-0.5 to 1.54-1.68 g/cm^3 (with 1.84 g/cm^3 in regions) in 26-50 h, over ten times faster than in IICVI. Improved disk-to-disk uniformity is achievable through optimized end-insulation and coil design. Initially the interior regions of the disks were hottest[3]. With time, the disk temperatures increased and the temperature difference between the i.d. and o.d. decreased[3]. The precursor gas-phase diffusivity was high, resulting in a densification front proceeding from the inside regions of the preforms towards the external surfaces (Fig.3). Regions which had densified less tended to catch up with the denser regions. The final density uniformity within a disk was within ±(5-8)%. The overall precursor conversion efficiency was 20-30%, over ten times that in IICVI and higher than in forced-flow, thermal-gradient CVI[4] of C. Under the appropriate conditions, no surface crusting occurred and the total amount of liquid tar by-product was much less than 1% of the incoming C_5H_{10}; no solid or powdery soot was found in any run. The rough-laminar carbon microstructure, which has excellent friction and wear properties, was obtained; undesirable isotropic carbon was not found. The compressive strength at 1.79 g/cm^3 was 268 MPa, considered very good. Other advantages of single-cycle, inductively-heated, thermal-gradient, isobaric CVI include: (1) Multiple preforms (even with different thicknesses) can be densified in the same run; (2) All process conditions, including temperature, pressure, flow rate and precursor dilution are fully adjustable in real time; lower pressure results in higher gas-phase diffusivity and is considered conducive to obtaining uniform density profiles and formation of matrices and composites with desirable properties; (3) Real-time monitoring and control of densification rate and process end-point were accomplished; (4) No fundamental technical barriers exist in scaling up both the preform size and the number of preforms per run; the method is well suited for small or medium batch size for "just-in-time" production; (5) Other materials, e.g. Al, B, TiN, SiC-C, SiC-SiC, and ZrO_2, singly or in combination, can be densified; to exploit the inherent speed of this process, the preform or the matrix needs to be sufficiently electrically conducting at the densification temperature to couple to the electromagnetic field (the frequency of the latter can be adjusted to the material system and dimensions); (6) No special fixturing or extra machining is required as in forced-flow, thermal-gradient CVI[4]; (7) There is no need to immerse the preforms in a flammable liquid[5] and the reactor can be located in a normal setting. *The work at AlliedSignal, Inc. was funded by the AlliedSignal Aerospace Co., Aircraft Landing Systems, South Bend, IN (D. Hayes, J. Pigford, J. Hendricks and N. Murdie).*

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Table 1. Published characteristics of chemical vapor infiltration methods used to densify refractory composites.

CVI Process	Preforms		Process			Reactor	
	Many	≥2.5 cm, all directions	Densification time*	Pressure adjustable	Precursor efficiency	Capital cost	Complex fixture
Isothermal Isobaric	Yes	Yes	V. long	Yes	Low	High	No
Plasma-Enhanced Low-Pressure	Yes	No	Long	Ltd.			
Early Thermal-Gradient Radiantly- or Inductively-Heated Isobaric	Yes[7]	No[7]	Long	Yes			Yes
	No[8]	Yes[8]	Long	Yes			Yes
Recent Thermal-Gradient Inductively-Heated Isobaric	Yes	Yes	Short	Yes	High	Low	No
Liquid-Immersion Thermal-Gradient Inductively-Heated Isobaric Atm.-Pressure	No	No	Short	No			
Forced-Flow Isothermal	No	No	Long	V. ltd.	High	Low[9]	Yes
Pulsed-Pressure Isothermal	Yes	No	Long	Yes			
Forced-Flow Thermal-Gradient	No	No	Short	V. ltd.	High	Low[9]	Yes
Catalyst-Enhanced Isoth. Isobaric	Yes	No		Yes		High	No
Particle-Transport-Enhanced (not for continuous-fiber composites)	No	Yes	Short	Yes			Yes

* with respect to preform thickness

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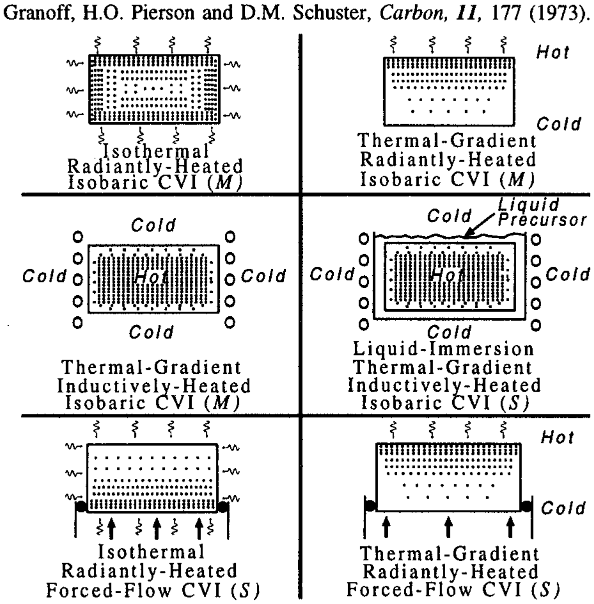

Fig. 1. Principles of the main published CVI methods, illustrated for one preform (augmented from[6]). Published *Multiple* or *Single* preform processing is so indicated.

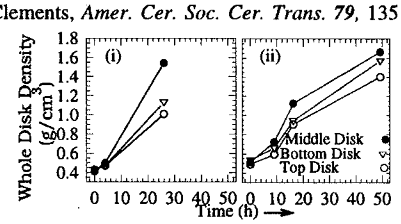

Fig. 2. Kinetics of inductively-heated thermal-gradient CVI[3]: (i) one set of preforms without insulation, *with* flow-channeler; (ii) three sets of preforms with insulation, *without* channeler. Lines are an aid to the eye.

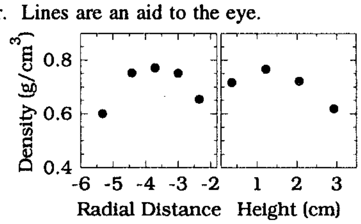

Fig. 3. Spatial density profiles in the middle C-C disk of a three-disk stack infiltrated for 9 h by inductively-heated thermal-gradient, isobaric CVI[10].