

RAPID DENSIFICATION OF INDUCTIVELY-HEATED CARBON-CARBON BY NOVEL THERMAL-GRADIENT, ISOBARIC CHEMICAL VAPOR INFILTRATION

I. Golecki, R.C. Morris, D. Narasimhan and N. Clements

AlliedSignal Inc., Corporate Research and Technology, 101 Columbia Road, Morristown, NJ 07962.

SUMMARY

Using a novel patented method [1], porous carbon-carbon (C-C) preforms, 4.25" od x 1.75" id x 1.2" thick have been densified in a one-cycle, 26 h process. The disks are heated by induction, creating an inside-out thermal gradient, and are exposed to cyclopentane vapor in a water-cooled vacuum chamber. This approach allows significantly higher operating temperatures (by 200°C+) compared to isothermal CVI. Rough-laminar carbon microstructure is obtained. Overall disk density of 1.68 g/cm³, with 1.84 g/cm³ in regions is measured, depending on process conditions. The compressive strength is 268 MPa at 1.79 g/cm³. The densification rate and end point are monitored in real time. The precursor utilization efficiency is 20-30%, the amount of tar generated is very small and no measurable soot is observed. Our process has significant scale-up potential, is economically competitive and can be used in other materials systems.

INTRODUCTION

Refractory composites, such as C-C, offer advantages of low density and excellent mechanical and thermal properties, especially for uncooled high-temperature applications, e.g., aircraft brake pads and engine components [2]. One of the most common fabrication methods of such composite structures is densification of a porous body having the desired shape by means of chemical vapor infiltration (CVI). A stream of precursor vapor flows over the part, which is kept at a temperature sufficient to decompose the precursor and produce the desired element or compound within the pores of the part, thus increasing its density. The deposition rate usually increases exponentially with increasing substrate temperature (with a ≈ 4 eV/molecule activation energy for carbon) and moderately with increasing precursor partial pressure. In a common application of CVI, a large number of porous carbon substrates are densified through exposure to a reactant gas (e.g., methane) in an enclosure uniformly heated to a temperature of about 1000°C. This approach, known as hot-wall CVI, requires an extremely long CVI time of 600-2000 h to achieve the desired density. The process must also be interrupted several times to permit grinding of the exterior surfaces of the substrates in order to open the pores and allow further infiltration. It is clearly desirable to reduce the processing time. However, increasing the pressure and/or temperature beyond certain ranges may produce unwanted homogeneous nucleation of powders in the gas phase, premature surface crusting and undesirable microstructure.

NOVEL METHOD AND APPARATUS

The main part of the water-cooled, stainless steel deposition chamber (Fig. 1) is 15" id x 17" high. The cyclopentane (C₅H₁₀) precursor enters the chamber as a vapor through a calibrated, mass-flow-controlled gas line maintained at 70°C [3]. C₅H₁₀ is a liquid at 25°C (vapor pressure = 321 Torr); its boiling point is 50°C. In large quantities it costs \approx \$ 0.44/kg [3]. The porous preform disks, each 4.25" od x 1.75" id x 1.2" thick, are

made of non-woven PAN [2] carbon fibers and have an initial geometric density in the range 0.4-0.6 g/cm³. The disks are placed around a Mo or Al₂O₃ mandrel inside a water-cooled copper coil, which is connected to an audio-frequency power supply. The disks are heated by induction; an electrically conductive mandrel is not required, as the conductivity of these C-C preforms is sufficiently high to couple directly to the electromagnetic field. Multiple disks can be infiltrated simultaneously; the results described here were obtained with three disks per run. In order to reduce radiative heat losses, grafoil plates were placed above and below the mandrel. In some runs, an 18.5" high quartz tube was inserted between the C-C disks and the coil, as a flow channeler for the C₅H₁₀. In other runs, a much shorter, 4.5" high quartz tube was placed between the bottom of the chamber and the coil, so that the od surfaces of the C-C preforms stared directly at the coil and chamber walls. The temperatures of the C-C disks were measured with 10 mil dia., Pt/13%Rh-Pt thermocouples inserted at different locations half-way through the thickness of the disks. The densification rate was determined in real time. The power and frequency of the induction power supply (8.8-13.2 kW, 4.9-8.6 kHz), total pressure (20-100 Torr) and C₅H₁₀ flow rate (170-540 sccm) were controlled during carbon CVI runs.

RESULTS AND MECHANISM OF DENSIFICATION

Average carbon pick-up rates per disk of 9.5 g/h or 10.6%/h were measured (Fig.2). The whole-disk density was increased from 0.41 to 1.541 g/cm³ in just 26 h, an average rate of increase of 0.044 g/cm³.h. Disk densities of 1.68 g/cm³ were obtained, compared to 1.80 g/cm³ for Poco graphite. The shape of the density vs. time curves was sigmoidal-linear rather than the much slower exponential approach to final density in isothermal CVI. Generally, the highest density was found in the middle disk in the stack, due primarily to lower temperatures at the outer surfaces of the two extremal disks. Improved end-insulation and optimized coil design will reduce such axial disk-to-disk variations, especially in a scaled-up stack, where the two

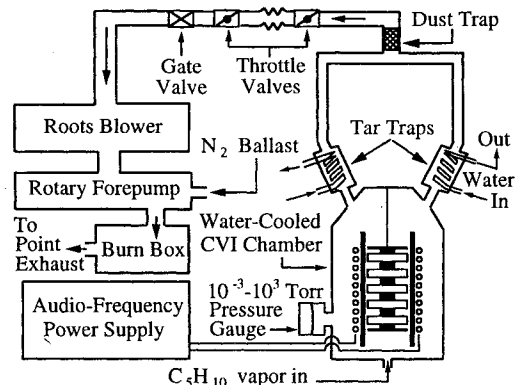


Figure 1. Simplified schematic diagram of AlliedSignal patented thermal-gradient CVI reactor.

extremal disks represent a very small fraction of the total. The density uniformity within a disk, measured from cored and sliced samples, was within $\pm(5-8)\%$. The overall utilization efficiency of the precursor, i.e. the amount of carbon added to the disks divided by the amount of carbon which flowed as C_3H_{10} , was 20-30%. Higher efficiencies were generally obtained with the long flow-channeler. The microstructure of the deposited carbon, as determined from the extinction angle of the Maltese cross in polarized-light microscopy [2], was rough-laminar ($19-23^\circ$), smooth \rightarrow rough-laminar ($13-15^\circ$) or smooth-laminar ($10-12^\circ$), depending on processing conditions. The rough-laminar structure is generally desired for braking applications. Isotropic carbon (0°) was not found. The compressive strength, measured for 0.26" diameter x 0.31" long samples, increased steeply with increasing density [3] and reached 268 MPa (39 ksi) at 1.79 g/cm^3 , which is considered very good.

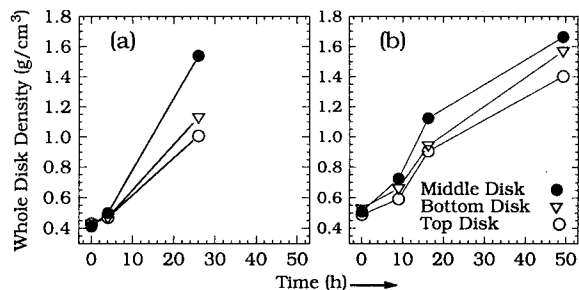


Figure 2. Carbon disk density vs. time in thermal-gradient CVI: (a) One set of disks (without grafoil insulation), with long flow-channeler, (b) Three separate sets of disks (with grafoil insulation), without long flow-channeler.

From Fig. 3, it is seen that the id region of the C-C preform disk was hottest initially, all three temperatures increased as a function of time and the temperature difference between the id and od decreased as a function of time. Temperatures inside the disk reached almost 1200°C , significantly higher than in isothermal CVI. Some surface crusting was noted and yellow vapors were observed in the chamber towards the end of this run. In those CVI runs which were stopped earlier, however, no surface crusting occurred, no yellow vapors were seen and the total amount of liquid tar was significantly smaller compared to the estimated 1-3% of the incoming C_3H_{10} for runs which were continued past surface crusting. No solid or powdery soot was found in any of the runs. In this thermal-gradient CVI process, the substrates are Joule heated by circumferential induced currents flowing inside them. The induced power is initially highest near the od and diminishes to zero in approximately 3δ , where the skin depth $\delta = 5(\rho/f)^{0.5}$, with δ in cm, the electrical resistivity ρ in $\text{m}\Omega\cdot\text{cm}$ and the frequency f in kHz. The temperature distribution in the substrates is dominated by the radiation losses, $\Delta Q = \epsilon\sigma_0(T_{\text{od}}^4 - T_{\text{wall}}^4)$, to the water-cooled coil and walls, with ΔQ in J, ϵ the emissivity (between 0 and 1), $\sigma_0 = 5.67 \times 10^{-8} \text{ J/K}^4\text{m}^2\text{s}$ the Stefan-Boltzmann constant and T in K. Thus, the temperature will initially be highest in the interior regions of the preforms, lower at the top and bottom surfaces and lowest at the od. The gas-phase diffusivity of the precursor is high, ensuring that the initial densification rate will be highest in those hottest interior regions, consistent with our density distribution measurements (to be published). An electrically

conducting mandrel results in additional heating near the id of the preforms, but does not change this general picture. With the long quartz flow-channeler, T_{wall} is in the range of $300-800^\circ\text{C}$, instead of $20-50^\circ\text{C}$. As densification progresses, the electrical (and thermal) conductivity of the preform increases, resulting in a shallower skin depth and improved coupling to the coil, i.e. higher induced current and higher temperatures near the exterior surfaces of the preform, as measured. Thus an "inside-out" densification front exists in the preforms.

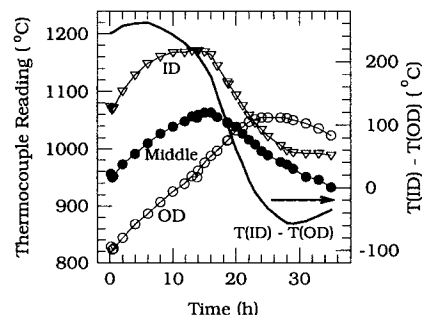


Figure 3. Time evolution of the temperature in three radial locations inside the middle disk in a carbon thermal-gradient CVI run with the long flow channeler.

CONCLUSIONS

Our novel patented [1] thermal-gradient CVI technique reduces the total densification time of porous C-C preforms by over a factor of ten compared to isothermal CVI, via the use of higher operating temperatures in the interior regions of the preforms and other innovations. No dipping in flammable liquids [4] and no special fixtures or machining are required [5], and the pressure is adjustable. There are no fundamental technical barriers to scaling up the substrate diameter and the number of substrates per run and the CVI time can be further shortened through optimization. Other materials, singly or in combination, can be densified using our method, including metals, semiconductors and room-temperature insulators, e.g. Al, B, TiN, SiC-C, SiC-SiC, and ZrO_2 . 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 which can be adjusted to the specific materials and dimensions.

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