IMPREGNATION/DENSIFICATION OF CARBON-CARBON COMPOSITES

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INTRODUCTION

Carbon-carbon composites are the most promising materials for high-temperature applications. Their thermal and mechanical properties have significantly improved thanks to the addition of reinforcing fibers to the bulk carbon. This has allowed carbon-carbon composites to be successfully used in various engineering applications. These include military, aerospace, industrial, commercial and medical applications [1,2,3,4].

Carbon materials can exhibit a very wide range of structures and textures, ranging from near amorphous to polycrystalline graphitic structures, which are controlled by the nature of the precursor material, the method of processing to carbon, and the ultimate heat-treatment temperature used in this operation [5]. These different structures and textures can lead to different composite properties and the widely different physico-chemical properties of the precursors themselves lead to a variety of processing options [6,7,8].

In general a carbon-carbon composite material consists of a carbonaceous matrix reinforced with carbon fibers in the form of continuous filament yarn, cloth, chopped fibers or three-dimensional woven reinforcements. Many different architectures have been used for the reinforcement of carbon-carbon composites. These include random fibers, unidirectional fibers, braided yarns. stacked 2-D fabrics, pierced fabrics to provide increased interlaminar shear properties, orthogonal 3-D geometries in either cartesian or cylindrical coordinates, or in multidirectional weaves designed to improve the off-axis properties and to maximize the empty spaces that occur at filament cross-over locations [9,10]. The combination of matrix with carbon fibers as well as the various architectures produce extraordinary properties which characterize this class of materials [11,12]. These include superior stiffness, better fatigue strength, high heat resistance, low shrinkage, low thermal expansion coefficient, high heat-storage capacity, pseudoplasticity and good chemical resistance [13,14,15,16,17]. Their disadvantages are the sensitivity to the oxidation and the complicated and expensive manufacture [18].

Carbon-carbon composites are manufactured usually from the carbon fibers (composed to the required form) and from the precursor of the matrix. Synthetic thermosetting resins or petroleum and coal tar pitches are used as the precursors of the matrix. The problem is that the matrix has after carbonization a very high porosity, therefore the densification process is necessary. There are two main densification techniques: the Chemical Vapour Deposition (CVD) and the Liquid Impregnation Process (LIP) [7].

CHEMICAL VAPOUR DEPOSITION

Chemical vapour deposition (CVD) is a process in which a solid product nucleates in the border layer and grows on a substrate, by decomposition or reaction of gaseous species, and involves the heating of a fibre preform in a gaseous environment so that the matrix is deposited from the gas phase. The technology developed up to now allows us a fine control of the composition and morphology of the solid deposit. Well-processed CVD-derived composites generally possess excellent mechanical properties as a consequence of the slow, steady build-up of the matrix material around the fibre network. The major drawback of CVD is the very slow rate of deposition leading to large material/energy inputs and a high final cost [19]. Several scientists active in the field refer to CVD densification of composites as Chemical Vapour Infiltration (CVI). The purpose of this nomenclature is to distinguish the deposition of material in the fibre preform from the simple layer deposition techniques used in the semiconductor and coatings industries. It will become apparent throughout the text that the deposition of material within the pore system of a fibre preform imposes severe kinetic limitations on industrially operated CVD processes [20].

The CVD process uses volatile hydrocarbon compounds such as methane, propane, benzene and other low-molecular-weight units as precursors. The technique is limited by both the kinetics of deposition and diffusion of the reactant gas within the structure. Carbon is deposited on the external and internal surfaces of the porous preform [2,7,20].

The fibre preform will have an initial pore structure dependent on fibre form, its content and arrangement. It is essential that the matrix material must be deposited throughout the pore structure, if a strong dense composite is to result. The reactant must diffuse through the boundary layer of laminar flow around the preform, diffuse into the pores and then be adsorbed and react. The products must be desorbed, and diffuse back out of the pores along the same route (pore and boundary layer) [21,22]. If the surface chemical reaction, needed to produce a solid deposit, occurs rapidly with respect to the diffusion process, the deposition will occur near the mouth of the pore rather than along it, rapidly sealing off the pores. Closed porosity is created which results in concentrating mechanical stress and is thus detrimental to the mechanical properties of the composite (figure 1*a*). If, on the other hand, such conditions are chosen that the surface reaction rate is a good deal slower than the diffusion rate, deposition can occur evenly along the length of the pore, to give a well-densified material (figure 1*b*) [4,20].

Densification of carbon-carbon composites by the CVD technique can be achieved by three main methods. The first method is the isothermal one. Under selected conditions the reacting hydrocarbon gas diffuses into the open pores of the preform depositing its carbon content on the surfaces of the preform. The carbon deposits produced by this method are of high density, high modulus and are highly graphitizable. In the second method, called the pressure gradient method, a pressure differential is created along the thickness of an isothermally heated preform. The hydrocarbon gas is forced to infiltrate through the open pores of the preform. The pressure differential reduces the infiltration time of the hydrocarbon and produces a uniform carbon deposit on the substrate of the preform. The third method is based on maintaining a thermal gradient across the thickness of the preform. The pressure inside the furnace is kept at the atmospheric level [23,24]. The hydrocarbon gas flows through the preform surface. The preform is kept at a temperature below the threshold pyrolysis temperature of the gas. The hydrocarbon gases then diffuse through the substrate providing carbon deposition on the inner surface of the substrate. The thermal gradient method is generally faster than the above mentioned two methods, but has a low reproducibility. Savage [20] mentions further methods: pulse CVD methods and miscellaneous methods.

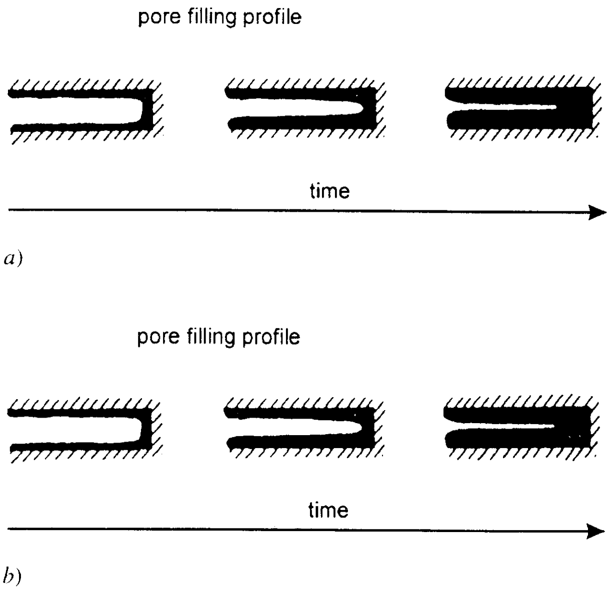

Figure 1. The balance of diffusion and surface reaction kinetics; idealized depictions.
a) surface reaction rate >> diffusion rate, *b)* diffusion rate >> surface reaction rate [20].

LIQUID IMPREGNATION PROCESS

Fabrication of carbon-carbon composites by the Liquid Impregnation Process (LIP) involves the impregnation of the preform structure with organic materials (precursors) and recarbonization. Thermosetting resin and high char yielding pitches are the two categories of liquid precursors (figure 2). When a combination of precursors is used, two different phases of the matrix are obtained. The morphology and the texture of the matrix depend on the precursor type, on the method of its application, on the spatial arrangement and on the number of the impregnation-recarbonization cycles [7,25,26,27].

The desirable features of the matrix precursor will depend on the processing procedure to be adopted and the characteristics and properties required in the final matrix will be determined by the applications for which the composite product is intended [29]. Nevertheless, given that the major applications are likely to involve mechanical and thermal stresses over a wide range of temperatures, the following characteristics would appear to be desirable:

Precursor - high volumetric yield of carbon,
- ability to penetrate into the fibre preform,
- ability to wet fibres,
- controlled rheology during pyrolysis.

Carbon matrix - low internal porosity,
- high strength and toughness,
- high strain to failure,
- high oxidation resistance,
- high thermal conductivity [5,6].

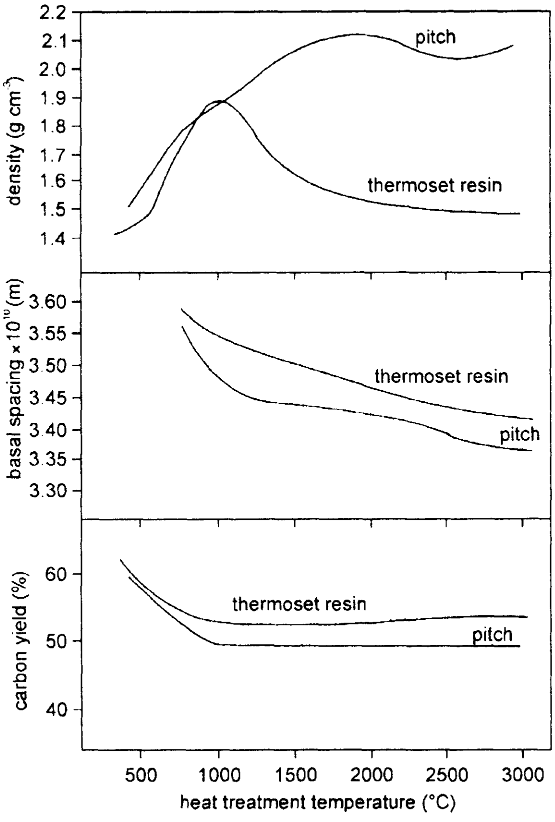

Figure 2. Characteristics of resin and pitch as a function of HTT [20].

Thermosetting resins are used as carbon matrix precursors because they are relatively easy to handle with materials with which to impregnate fibres and because a large technology base exists for their use in the composites industry [30]. All of the methods proved in this domain such as filament winding, prepreg, hand lay-up or pultrusion may be employed to produce large artefacts of complex geometry. Thermosetting resins polymerize at low temperatures (< 250 °C) to form a highly three-dimensionally cross-linked non-melting amorphous solid. A glassy, isotropic carbon is formed upon pyrolysis, which does not graphitize even at temperatures up to 3000 °C. The carbon yields obtained from suitable thermoset precursors usually vary between 50 and 60 wt.%. The low density of the carbon formed (~1.5 g cm^{-3}) may preclude its use in certain applications, but there are many applications where a strong, non-graphitic matrix is desirable. At very high temperatures (> 2000 °C) shrinkage stresses at the fibre-matrix interface can cause glassy carbon matrices to graphitize. The resin impregnation method, by virtue of the low carbon yields generally obtained, must follow up three steps to completion:

1. To impregnate fibres and form the basic shape.
2. To carbonize to form a porous carbon structure.
3. To reimpregnate/carbonize to improve the density and hence the properties.

In most cases, multiple densification cycles will be required before the component is complete. The carbon yields of 50 - 60 %, achieved with thermosetting resins, although low, represent a conversion efficiency of around 95 % of the carbon actually available [25,26].

Pitches are attractive precursors of carbon matrices because they can give high carbon yields, are graphitizable, and can be used to design directionality into the matrix as well as in the fibres. Thus, under certain circumstances, the matrix microstructure and properties can augment those of the fibres in the fibre direction. Pitches are thermoplastic systems. This thermoplastic character can be made use of in the fabrication process, but it can also cause problems in the pyrolysis stage when the pitch may have very low viscosity and exude from the fibre preform or cause bloating to take place when the volatile products of thermal degradation are released [31]. It is thus important to understand the physico-chemical properties of pitches and their pyrolytic products both before and during the carbonization process if effective control is to be exercised over the fabrication operation. When carbonized, they pass through a liquid crystal phase, known as mesophase, eventually forming a high-density (~2.0 g cm^{-3}) graphitic carbon at high temperatures (> 2300 °C). At atmospheric pressure the carbon yields obtained from pitches are disappointingly low at around 50 wt.%, i.e. similar to those from high yield thermosetting resins. The application of high pressure during carbonization results, however, in yields of up to 90 % . Furthermore, the application of high pressure eliminates the bloating observed during the ambient-pressure carbonization of pitch-carbon-fibre composites, resulting from the low melt viscosity of the pitch matrix [33]. At very high pressures (200 MPa) the coalescence of the mesophase necessary to produce good-quality carbon-carbon does not occur, so as optimum the value of around 100 MPa is generally chosen for the high-pressure processing of carbon-carbon composites [7,25,26].

CONCLUSION

The carbon-carbon composites can be densified by two different processes, namely, Chemical Vapour Deposition (CVD) and Liquid Impregnation Process (LIP). In general, CVD processing techniques produce composites of higher density, stronger bonding between the carbon deposits and the reinforcements. This enhances their mechanical properties. Economical considerations and the bottleneck pore closing problem make the LIP superior to the CVD technique.

The CVD and the LIP processes can be used for improving the thermal resistance of carbon-carbon composites. The matrix of these composites should involve employ SiC, ZrC, TiC or NoC.

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