THE INFLUENCE OF COAL TAR PITCHES ON 5D C/C COMPOSITES OBTAINED BY VACUUM IMPREGNATION/CARBONIZATION PROCESS

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Introduction

Carbon-carbon composites (C/C) are produced by multi-step processes, which involve the preparation of carbon fiber preforms (CF), followed by cyclic and successive carbon impregnation/heat treatments [1]. The final C/C performance depends mainly on the CF preform characteristics, carbon matrix microstructures, as well as the interaction of these two components during the forming process [2]. The preform densification with pitches is commonly performed by costly process, where high pressure is associated with high temperature, aiming at increase in carbon yield during each cycle [1]. The present paper reports the C/C properties obtained by vacuum impregnation/carbonization (V-I/C) [3] performed over the weaved 5D preform, using two different coal tar pitches, with and without mesophase.

Experimental

Two commercially available coal tar pitches, namely pitch M and N, with and without mesophase spheres, respectively, both with softening point (SP) 110°C, were chosen as impregnant materials. The general properties of these pitches are : pitch M : Anisotropy (Aniso) = 11%; quinoleine insoluble (QI) = 9,2 %; toluene insoluble (TI) = 37,7 %; coking value (CV) = 59 %; and, pitch N : QI = 12,1 %; TI = 31,9 %; CV = 56 %.

The preform was prepared by manual weaving using the CF T300-6K roving, without surface treatment. The fiber bundles were previously coated with a mixture of phenolic resin (resafen 12010) and 325 mesh natural graphite (10%). This resin coated CF bundles were weaved in five directions, four coplanar 45° directions at XY plane, and one in Z direction orthogonal to this plane. The weaved skeleton was heat treated up to 180°C,resulting a 5D preform with 33 vol. % of CF content and with average density of 0,65 g/cm^3. The densification cycles were performed by a sequence of V-I/C, carbonization (HTC) and graphitization (HTG) treatments. The V-I/C processes were done at 650°C/1h at about 80 kPa. The complete HTC and HTG of samples were performed respectively, at 1000°C under N_2 atmosphere, and at 2500°C under argon atmosphere. The densification cycles were repeated on each sample till the saturation of mass gain was observed.

The bulk densities (*d*) were determined after each densification cycle. The polished surfaces of C/C samples were analyzed using optical microscopy (OM). These surfaces were then etched by chromic acid for SEM examination. A commercial synthetic graphite was used as standard for comparative analysis of C/C physical properties. The electrical resistivity (ρ) was measured by four point method and the thermal expansion coefficient (CTE) by thermomechanical analysis. Due to the reduced size the samples of about 35 mm in length, the Young's modulus (E) were determined by sonic method and flexural strength (σ) by three point bending using 20 mm span.

Results and Discussion

The figure 1 shows the bulk density variation of 5D C/C as function of densification cycles for both pitches. It shows that the impregnation efficiency of both is similar, giving the C/C with close density values.

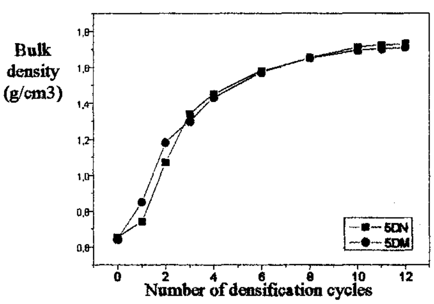
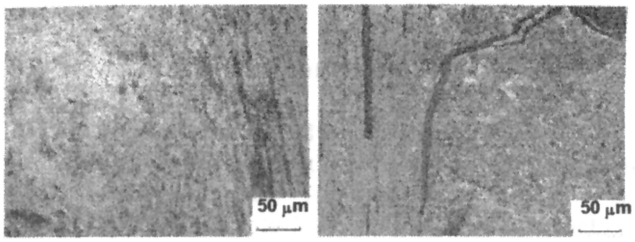


Figure 1. The bulk density variation of 5D C/C as function of number of densification cycles.

Microstructure analysis by OM of these samples showed clearly that the coke matrix texture varied as function of pitch type, as can be seen in figure 2. The composite 5DN, obtained from pitch N, exhibited an anisotropic carbon matrix with isotropic carbon islands. While the 5DM exhibited a wholly homogeneous anisotropic coke matrix, with larger optical domain. It was also showed that there is no infiltration inside the fibers bundles.

The physical properties of C/C samples and synthetic graphite (PSG) determined under the same conditions, are presented in the Table I.



(a) (b)

Figure 2. Optical micrographs of 5D C/C composites: (a) 5DM and (b) 5DN .

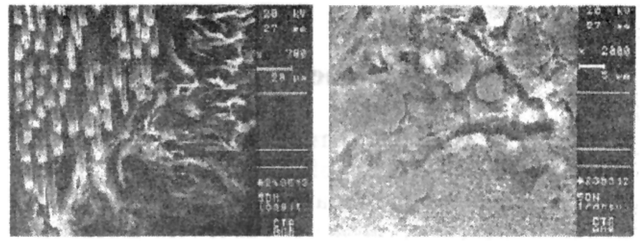
Table I. Properties of C/C and commercial PSG.

Properties	PGS Long.	5DM XY	5DN XY
d (g/cm^3)	1,78 ± 0,01	1,72 ± 0,03	1,75 ± 0,03
ρ (10^{-3} Ω cm)	1,45 ± 0,02	1,18 ± 0,17	1,64 ± 0,17
CTE*(m/m°C)	5,3 x 10^{-6}	3,4 x 10^{-6}	2,1 x 10^{-6}
E (GPa)	12,8 ± 1,0	16,8 ± 4,0	13,1 ± 3,0
$\sigma_{flex.}$ (MPa)	58 ± 2	58 ± 2	55 ± 9

* Coefficient of Thermal Expansion - analysis done up to 400°C.

The composites 5DM and 5DN presented lower d than synthetic graphite, but their ρ and CTE values are lower, indicating their superior electrical and thermal properties. The higher value of σ_{flex} for synthetic graphite can be associated with polygranular characteristics and the span length used. Brittle materials have opposite effect to the composites when three point methods is used as function of span length [4]. From comparative analysis of the values in Table I, it can be shown that the pitch M leads to the production of C/C with higher electrical, thermal and mechanical properties than pitch N.

The detailed microstructure analysis, by SEM, is presented in figure 3. The figure 3 (a) revealed that the essentially anisotropic coke of 5DM matrix, observed by OM, is constituted mainly lamellar structures. The anisotropic coke with isotropic island of 5DN coke matrix, however, revealed to have large lamellar structures and small and thin lamellar randomly stacked in cluster form. These distinct carbon matrix structures probably have induced the differentiated modification of CF microstructures as can be seem from their micrographs, as a consequence of successive densification cycles [2]. The 5DM CF cross section showed higher reactivity for chromic acid, which implies the development of anisotropy in the fiber. This CF anisotropy probably is due to a fiber stress graphitization effect in an environment with essentially lamellar matrix [2]. The same effect was not observed in the CF of the 5DN composites. The fiber was more acid resistant and exhibited a skin core structure.



(a) (b)

Figure 3. SEM micrographs of 5D C/C etched by chromic acid: (a) 5DM and (b) 5DN .

Conclusions

From experimental results it can be concluded that both pitches have similar efficiency on densification of 5D preform by vacuum impregnation/carbonization process. The coal tar pitch with mesophase spheres and lower natural QI fraction content is more suitable to produce C/C composites with higher anisotropy carbon matrix and improved electrical and thermal properties. The flow textured matrix coke with large optical domain leads to the structure modification of carbon fiber which improves the C/C mechanical properties.

Acknowledgments

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