DEVELOPMENT OF ISOTROPIC CARBON-CARBON COMPOSITES FOR THERMAL MANAGEMENT

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Introduction

Carbon /Carbon composites are used in a number of applications in the space, defence and nuclear etc.(1) More recently they have become critical materials for thermal management purposes, as these materials can be tailor- made to suit the specific application. The most important property required for thermal management is thermal conductivity. In the case of C/C composites thermal conductivity can be suitably adjusted through the choice of fiber reinforcements, matrix carbon and processing conditions.

It is well known that high thermal conductivity composites can be developed using mesophase pitch based fibers and mesophase pitch matrix as both these components possess high Tc. Most of the reported values of Tc in literature pertain to continuous fiber based composites which exhibit anisotropic properties. There are applications which require isotropic thermal conducties of composites like Tokamek fusion Reactor (2)

Isotropic graphite i e. IG-11 has value of 120 W/m $^{\circ}$C whereas isotropic composites have values of upto 180 W/m $^{\circ}$C in each direction. There is some potential to increase these values to 250 to 300 W/m $^{\circ}$C which can be achieved by using : high Tc fibers and matrix, random distribution of fibers in all the three directions ,. developing large La values of the crystallites and achieving near zero porosity in composites.

C/C composites have been developed using different commercially available carbon fibres as reinforcements and coal tar pitch matrices possessing different softening points. They have been characterised in terms of microstructure, electrical resistivity, thermal conductivity and texture crystallite dimensions. Correlation's between microstructure and different properties have been elucidated.

Experimental

The green composites of size (40x30x3) mm were developed using chopped carbon fibers of size (2mm) and different type of Coal Tar Pitches (CTP) possessing different softening points were used as matrix precursor, using the matched mould die technique:

Reinforcements

F1 T-300 (Pan based CFs, κ =8.5 W/mK)

F2 HM 35 (Pan based CFs , κ = 90 W/mK)

F3 P-120 (Pitch based CFs, κ =640 W/mK)

F4 Dialed K13710 (Pitch based CFs, κ =140 W/mK)

Matrix

M1 Coal Tar Pitch (SP 105-109 C)

M3 Mesophase Pitch (Mitsubishi SP 285)

Composites were heat treated to 600 °C @ 5 °C /hr, and from 600°C to 1000 °C @ 10°C /hr,. The porous carbon composites were impregnated with coal tar pitch (SP 97-98 °C) at a pressure of 30 atms and heat treated to 600°C under pressure of 300 atms, further heat treated to 1000°C @ 10°C /hr and to 2600 °C in a graphitisation furnace. Composites were characterised for physical, electrical and thermal properties using mercury prosimetry, μ TA through AFM, microstructure using optical microscopy and X-Ray diffractrometry. μ TA (Micro Thermal Analysis) is an exciting new innovation(3,4) which combines the visualisation power of Atomic Force Microscopy (AFM) with the characterisation capabilities of thermal analysis. In Micro-Thermal Analysis , the AFM head is fitted with an ultra-miniature temperature probe which not only provides the heat source , but also measures the thermal response providing information similar to traditional thermal analysis, but on a microscopic scale.The instrument images the structure of a 100x100 μm region of the sample in terms of its topography, thermal conductivity, and thermal diffusivity. With a resolution of approx. 1μm, any point (2x2μm) on the image can be selected for characterisation.

Results and discussion

Table 1 show the physical properties of carbon/carbon composites heat treated to different temperatures respectively.

Density of the green composites varied from 1.28 to 1.60 g/cc , the maximum density being in case of F3M1 sample, density of F3 fiber being the maximum.(1.81 g/cc), volume % of fibers was 50 % in each sample. Density decreases on carbonisation as expected , the value being 1.12 to 1.33 g/cc. On impregnation and precarbonisation upto 600°C under pressure of 300 atms and carbonisation upto 1000°C under normal pressure, density of the samples increases significantly, average improvement being 22 to 25 % compared to an average improvement of 8 to 10 %. This is due to well known phenomena of increase of char yield under pressure(1). After graphitisation of the samples there is not much increase in the density of composites, the values remain all most unchanged.

Optical Microscopy of Composites

Fig. 1 shows the microstructure of the F3M3 (heat treated to 1000 °C) sample. Fibers are present in the ab plane in both the directions . The preferred orientation of these blue and yellow areas relative to the directions of the crossed polarisers indicates that the graphene layers of the matrix tend to allign parallel to the fiber surface, thus showing the development of anisotropy. The matrix present as bulk matrix is optically anisotropic with no preferred orientation of graphene layers. Microstructure of F3M3 (Fig.1) heat treated to 2600°C shows that the alignment of graphene layers along the fiber is more leading to development of large amount of anisotropy. Coloration of the anisotropic domains appeared plain and smooth, as a consequence of the occurrence of numerous slight misorientations within the domains, at a scale much lower than the resolution of the microscope (smooth laminar texture). On the

other hand, though most of the matrix areas were exhibiting the features above, i. e. large anisotropy, another aspect was found from place to place, where blue and yellow areas had tiny sizes and were randomly oriented. These areas are described as fine mosaic texture, which correspond to the association of very fine anisotropic domains, whose sizes are just above the resolution of microscope. There is development of annular gaps to a larger extent at fiber/matrix interface which indicates that bonding between fiber and matrix is weak.. One can see even the microstructure of fiber itself which is radial in nature as expected of a pitch based carbon fiber.

Electrical resistivity of Composites

Electrical resistivity of composite samples can give fair idea about the thermal conductivity of the sample as some striking correlation's have been observed between electrical resistivity and thermal conductivity of composites. A special set up for the measurement of resistivity of small samples of size 8 mm x 8 mm by four probe technique was designed and got fabricated. The set up was versatile in the sense that it was possible to measure voltage drop at various places for the same current. An average of at least 12-15 such measurements was used for calculations for the electrical resistivity of a particular sample. Table 2 gives the values of electrical resistivity of different samples along length as well as width direction.

Electricity resistivity decreases in the order of F1M1, F2M1, F3M1, F4M3 and F3M3 along length as well as width direction for carbonised composites but the values of ρ_1 and ρ_2 on average are same. For carbonised samples after impregnation the electrical resistivity decreases in the order of F1M1, F3M1, F2M1, F4M3 and F3M3 in both the directions. After graphitisation the values decrease in the order of F2M1, F1M1, F3M1, F4M3 and F3M3 in both the directions. The values in general decrease by a factor of 10 after graphitisation which is expected as there is development of crystallinity (increase in size of La and Lc) on heat treatment temperature. However the values of ρ_1 and ρ_2 even after graphitisation are approximately same. This indicates that the composite is isotropic in nature.

X-ray Diffractrometry of Composites

The above mentioned composite samples were characterised by X-ray diffraction for determination of crystallite parameters and d-spacing . Table 3 gives the average values of approximate crystallite dimensions of the composite samples. The d-spacing decreases in the order of F1M1, F2M1, F3M1, F4M3 to F3M3(3.3502 to 3.3392A) and the values of La and Lc increases in the same order respectively. This is expected as the crystallite dimensions of CFs decreases from Pitch based fibers to Pan based fibers. Pitch is graphitisable in nature and gives soft carbon on pyrolysis whereas Pan based fibers are amorphous in nature. Coal tar Pitch gives soft carbon on heat treatment. The values of La and Lc are 14.4, 17.5, 310 and 204.6A for F1M1 and F3M3 samples

respectively. The values of other samples are in-between these two samples as expected.

Thermal Conductivity of Composites

As the main objective of this study is to study the influence of processing and microstructural features on the development of thermal conductivity in Carbon/carbon composites. Prior to bulk thermal conductivity measurements, the samples were characterised by "thermal microscopy" using μ TA 2990 instrument which is a comparative method.

Figs 2 is a typical image that illustrates the topographic and thermal images of sample F4M3 . As this technique is qualitative in nature at present , darker images indicates less conductive and lighter images indicates more conductive. The values of thermal conductivity of different fibers are given in the experimental part .The Tc of F3 fiber is maximum (640 W/mK) and minimum for F1 (8.5 W/mK) fiber.In general the value of Pitch based fibers are more compared to Pan based fibers. The matrix (whether darker or lighter) will indicate the conductivity of the matrix portion. Carbon obtained from M3 matrix is lighter compared to carbon obtained from M2 and M1 matrices, indicating that matrix carbon is more conductive than M2 and M1 matrix carbons.

Conclusions

The studies clearly shows that the samples developed shows isotropic properties on macro scale within the plane. Thermal conductivity of Pitch based systems (F3M3 and F4M3) is more compared to Pan based systems, the system taken as model composites. These are only the initial results, detailed results with bulk thermal conductivity measurements will be published in carbon journal.

Acknowledgements

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Table 1 : Properties of carbon/carbon composites heat treated to different temperatures

Composite Type	Bulk Density of Composites (g/cc)				Kerosene Density (g/cc)	Porosity of graphitised composites
	green	carbonised	Impregnation+carbonisation.	Graphitised	Graphitised	(%)
F1+ M1	1-35 -1.40	1.15-1.18	1.45	1.51	1.79	15.3
F2+ M1	1.28-1.35	1.15-1.25	1.54	1.54	1.935	20.4
F 3+ M1	1.55-1.60	1.28-1.33	1.64	1.537	1.855	17.1
F3+M3	1.42-1.54	1.22-1.33	1.60	1.58	1.889	16.1
F4+M3	1.44-156	1.12-1.31	1.63	1.426	1.82	21.6

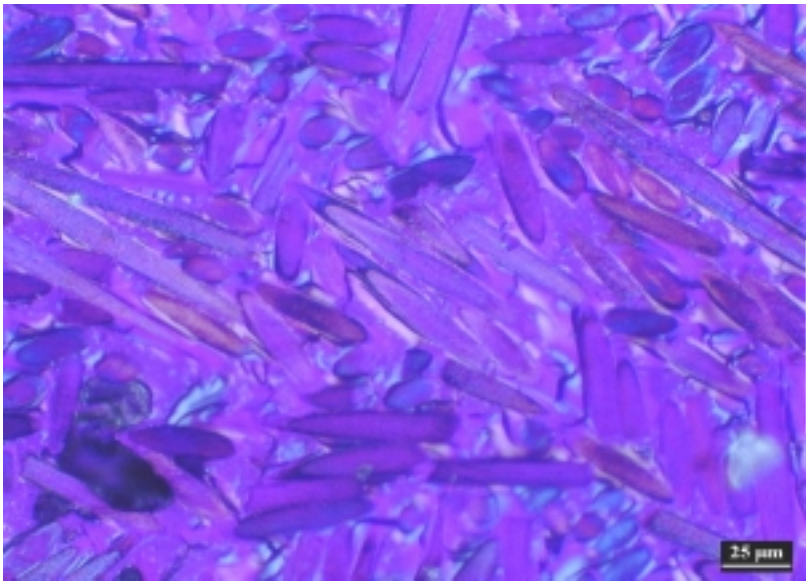
Table 2: Crystallites parameters of Carbon/Carbon composites

Sample	d_{002},nm	La, nm	Lc,nm
F1M1	0.3502	1.43	1.75
F2M1	0.3443	5.98	3.53
F3M1	0.3429	26.72	17.28
F3M3	0.3392	31.01	20.46
F4M3	0.3401	16.47	12.86

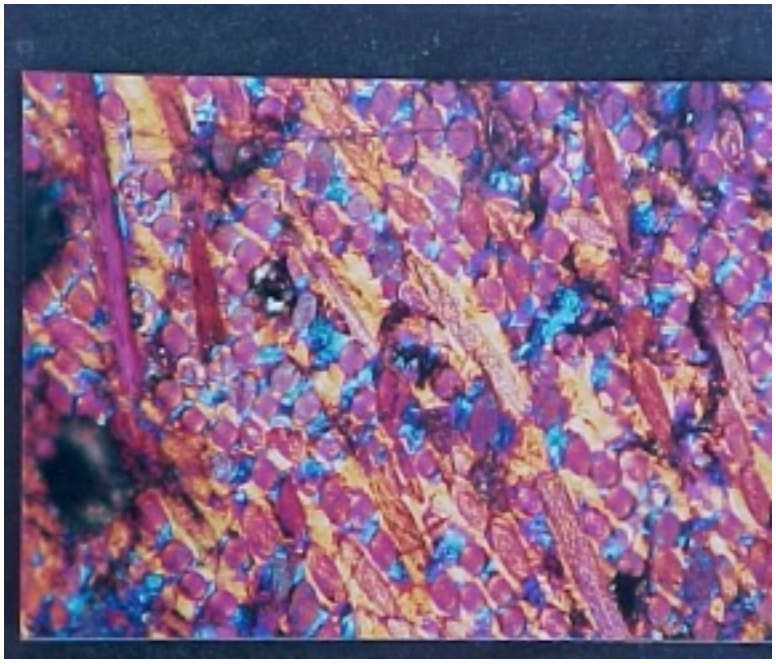
Table 3: Electrical properties of composites after heat treatment to different temperatures

Composite Type	Electrical resistivity of carbon /carbon composites (μ ohm cm) Carbonised		Impreg+carbonised		Graphitised	
	ρ_1	ρ_2	ρ_1	ρ_2	ρ_1	ρ_2
F1+M1	6.5-7.2	6.-6.5	3.2-5.6	4.5-5.2	0.63-1.84	0.75-1.48
F2+M1	5.1-5.2	5.7-5.8	3.4-4.4	3.6-4.3	0.86-1.72	0.63-1.59
F3+M1	3.0-3.5	4.5-5.0	2.3-3.2	4-4.5	0.7-0.9	0.71-1.2
F3 M3	2.5-3.0	2.5-2.7	2.0-2.4	2.8-3.0	0.5-0.93	0.53-0.7
F4M3	3.0-3.5	2.8-3.2	3.0-3.3	2.8-3.0	0.4-0.86	0.6-0.9

ρ_1 and ρ_2 values are the direction of length and width respectively



1000 C



2600 C

Fig1. Optical micrographs of F3M3 sample heat treated to 1000 C and 2600 C

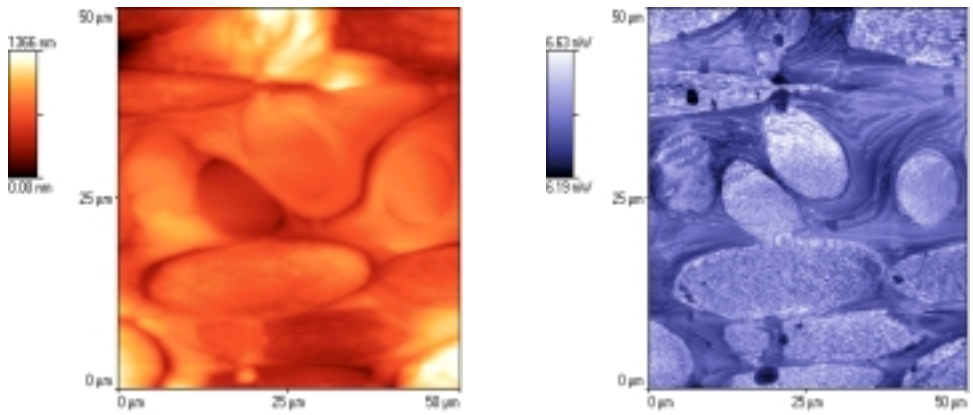


Fig.2 Topographical and Thermal image of F4M3 sample heat treated to 1000 C

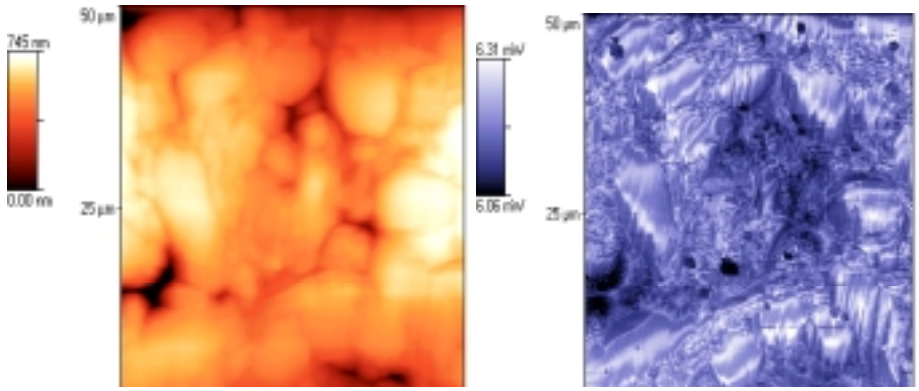


Fig.3 Topographical and Thermal image of F1M1 sample heat treated to 1000 C