DEVELOPMENT OF HIGH THERMAL CONDUCTIVITY CARBON-CARBON COMPOSITES USING VAPOR GROWN CARBON FIBRES AS REINFORCEMENT

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Introduction

Carbon – carbon composites are a family of advanced composite materials. They are the most advanced form of carbon and consist of a fibre based on carbon precursors embedded in a carbon matrix. This unique composition gives them such properties as low density, high thermal conductivity and shock resistance, low thermal expansion. The unique features and an advanced manufacturing technology which leads to a cheaper production process make this material more and more available for industrial applications.

Recent advances in the composites have established that these materials are an attractive candidate for thermal management applications [1, 2]. Vapor grown carbon fibre is a new class of fibres which is distinctively different from other types of carbon fibres in its method of production, its unique physical characteristics and prospect of low cost fabrication [3,4]. These fibres represent a variety of carbon fibres different from pitch based and polyacrylonitrile (PAN) based precursors. Characterizations have revealed that these fibres present exellent thermal and electrical conductivities [5, 6] greatly exceeding those of PAN based fibres.

Due to their unique physical properties and their potentially low cost of production these fibres are interesting for their possible application, principally as reinforcement in composite material [7, 8].

The measurement of thermal and electrical properties of VGCF based composites has become an important issue for the use of these composites in industrial applications [9]. Recently [10], it is observed that VGCF composites with phenolic resin matrix had low thermal conductivities (approximately 0.56 W/m K) indicating they were good insulating material.

The fabrication and characterization of VGCF composites with epoxy, poly (Phenylene sulfide), phenolic matrices are quite abundant in the literature [10 – 13]. But the fabrication and characterization of VGCF composites with binder coaltar pitch as a matrix is lacking in the literature. Therefore, an attempt has been made to undertake a systematic study to develop VGCF reinforced pitch matrix composites as a high thermal conducting material and correlate the fabrication condition i.e. changing volume fraction of vapor grown carbon fibres and their physical and thermal properties at room temperature.

Experimental

Vapor grown carbon fibres , Pyrograph-III , obtained from from M/s Applied Sciences, USA contained about 3% iron by weight as catalyst. These fibres were first refluxed with concentrated hydrochloric acid for 5 hrs to remove iron [14]. The removal of Fe was confirmed by TGA analysis of the fibres before and after the treatment. The catalyst free fibres were then further refluxed with 30% nitric acid for 3 hrs to incorporate surface functionality on the fibres. However, IR spectroscopy results do not show the band corresponding to oxygen containing functional groups e.g. C-O, C=O or C-OOH on the fibre surface. SEM micrographs, of these treated fibres also did not show any surface damage or etching. These fibres were used as reinforcement with coal tar binder pitch having softening point of 215˚ C.

 Green composites of size 18 mm dia and 5 mm thickness were prepared using different fibre volume fractions i.e. 20%, 35% and 50% , (designated as A,B and C respectively) by match mold die technique. The VGCF fibres and powdered pitch (-300 mesh) were mixed together in pestle and mortar to obtain homogeneous mix before molding.

The green composites A,B and C were heat treated to different temperatures ranging from 1000˚C ,1500˚ C and 2400˚ C in nitrogen atmosphere.

Structural development at different stages of heat treatment was determined by x-ray diffraction analysis of the powdered samples. Electrical resistivity data of the samples was used to estimate the thermal conductivity of the c/c composites.

Results and Discussion

Fig. 1 represents the changes in the bulk density of the samples at different stages of heat treatment temperatures with three different fibre volume fractions as discussed above. It is very interesting to note that the density of the composites increases with decrease in the fibre volume contents. Normally one would expect the density of the composite to be maximum with maximum fibre volume fraction since the density of VGCF is close to 2g/cc. The density of composite A and B is greater than 1.6 g/ cc, while that of composite C is less than 1 g / cc, even after HTT of 2400°C. The improvement in density in composites A and B shows strong interaction between fibre and the matrix, which is not the case with composite C. The observation is quite contrary to one observed for carbon-carbon composites developed with PAN or pitch based carbon fibres having diameter of the order of 6-8 microns [15].
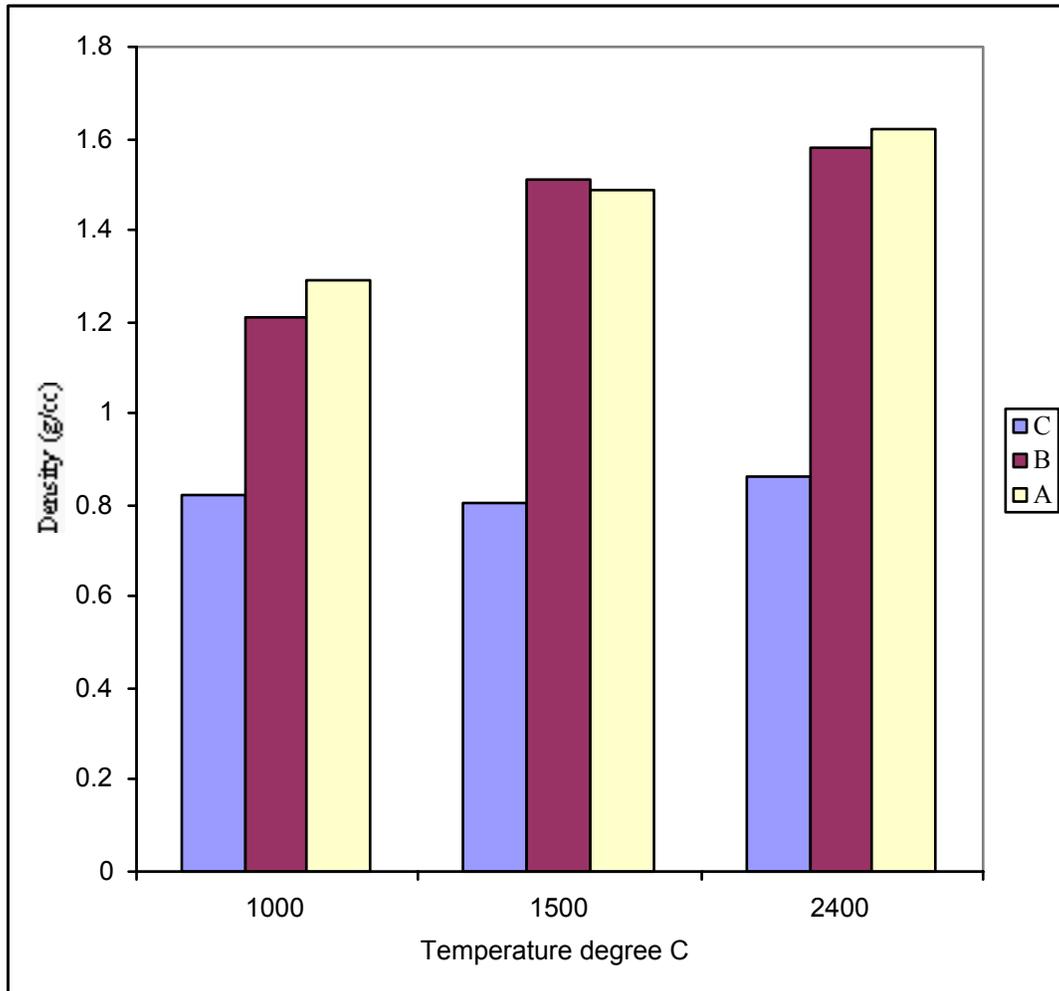
Figure 1. The change in density with heat treatment temperature of the composites A,B and C.

With the diameter of only 0.1 to 0.3 microns VGCF have much higher aspect ratio and correspondingly should offer very high volume fraction of interface in the composites. This therefore results into strong fibre matrix interaction even at volume fraction of as low as 20%. However, with higher volume fraction i.e. 50%, the fibres tend to agglomerate and the effective interface volume is therefore much lower as is evidenced in Figure 2. , showing lack of adhesion between fibre and matrix, so much so that the matrix tends to carbonize or graphitize independent of the fibre reinforcement. The matrix volume shrinkage during heat treatment therefore leads to considerable porosity in the composite volume. The density of composite C is therefore much lower than the composites A and B.
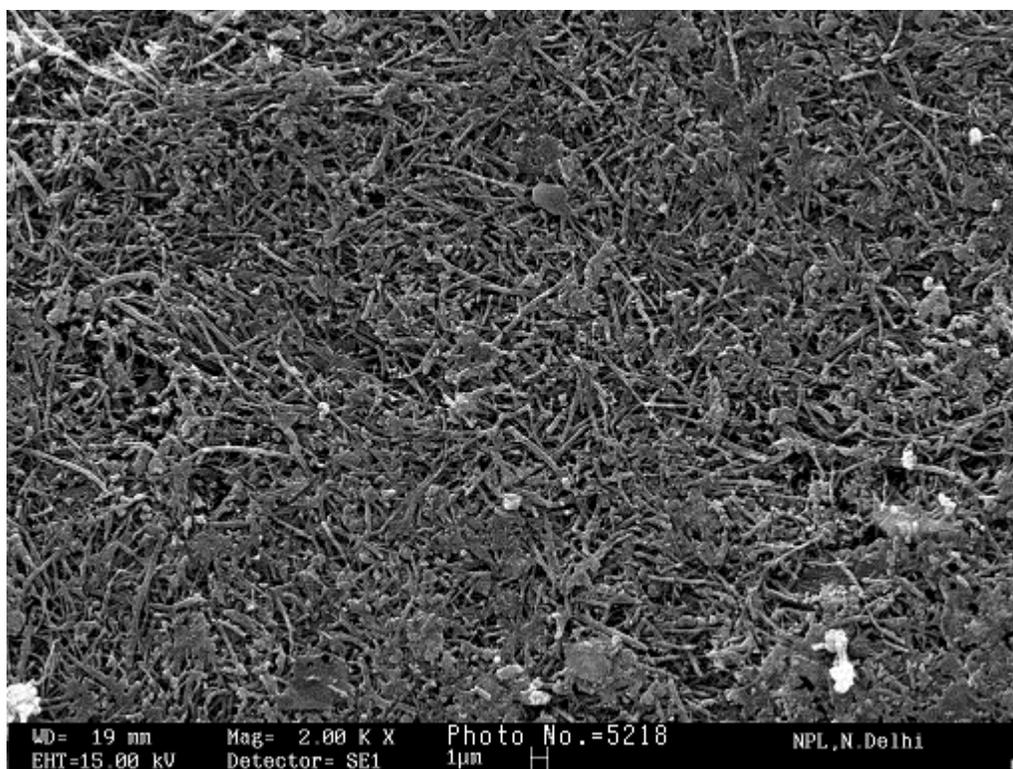
Fig.2 SEM micrograph of composite C

Table-1 shows the d_{002} values obtained from the XRD profiles of the c/c composites A-C heat treated to different temperatures.

Table 1 - Values of d_{002} spacing with heat treatment temperature

Sample code	d_{002} (Å)		
	1000 ° C	1500 ° C	2400 ° C
A	3.404	3.424	3.438
B	3.420	3.430	3.391
C	Work is in progress		

Quite interestingly, the d-values suggest that microstructure of composites A and B remain turbostratic in nature and practically there is no effect of the heat treatment temperature. Such type of structure reveals that the bonding between the VGCF and the pitch is so strong that the pitch is not allowed to graphitize during co-carbonization. Further, the distribution of individual filaments in the pitch matrix is quite homogeneous so that there are no regions of bulk matrix present in the composites A and B, which would show the structural features of a graphitized matrix like in composite C.

The above observation regarding the structure of the carbon - carbon composites were further established by the measurement of the electrical resistivity of individual composite. Fig. 3 shows the variation in the electrical resistivity of the composites measured across the molding direction. The resistivity of composite C is almost two orders of magnitude higher at 1000°C, which however, comes down appreciably with further heat treatment temperatures of 1500°C and 2400°C respectively to the order of 20 mΩcm. This confirms the observation that there are high contact resistances in composite C because of lack of available matrix around the fibres. The value of resistivity for composite C, however, becomes even lower than that for composites A and B respectively which is in the range of approx. 200 mΩcm at 2400˚C, the reason being that the matrix pitch in composite C is able to graphitize unlike for composites A and B . The result also suggests that the fibre matrix interactions in composites A and B are so strong at initial stages of carbonization that it does not allow any further structural transformations to take place even at heat treatment temperature of 2400°C. This effect has not been reported so far.

Since the fibre/matrix interactions in the composites A and B are so strong, one could assume these composites to be monoliths and thus estimate the thermal conductivity values from the famous electrical resistivity versus thermal conductivity curve reported by Issi [16]. Following the curve conductivities of composites A and B have been estimated to be 8 W/mK only. However, these results seem to limit the thermal conductivity of the composites which shows remarkable density during first step of carbonization(normally one would require two to three impregnation/carbonization cycles with PAN or pitch based carbon – carbon composites to achieve densities of the order of 1.6 g/cc.). The composite 'C' on the other hand, shows maximum electrical conductivity together with minimum density. The study has brought out new but at the same time contrary (to common belief) results which need further investigations.
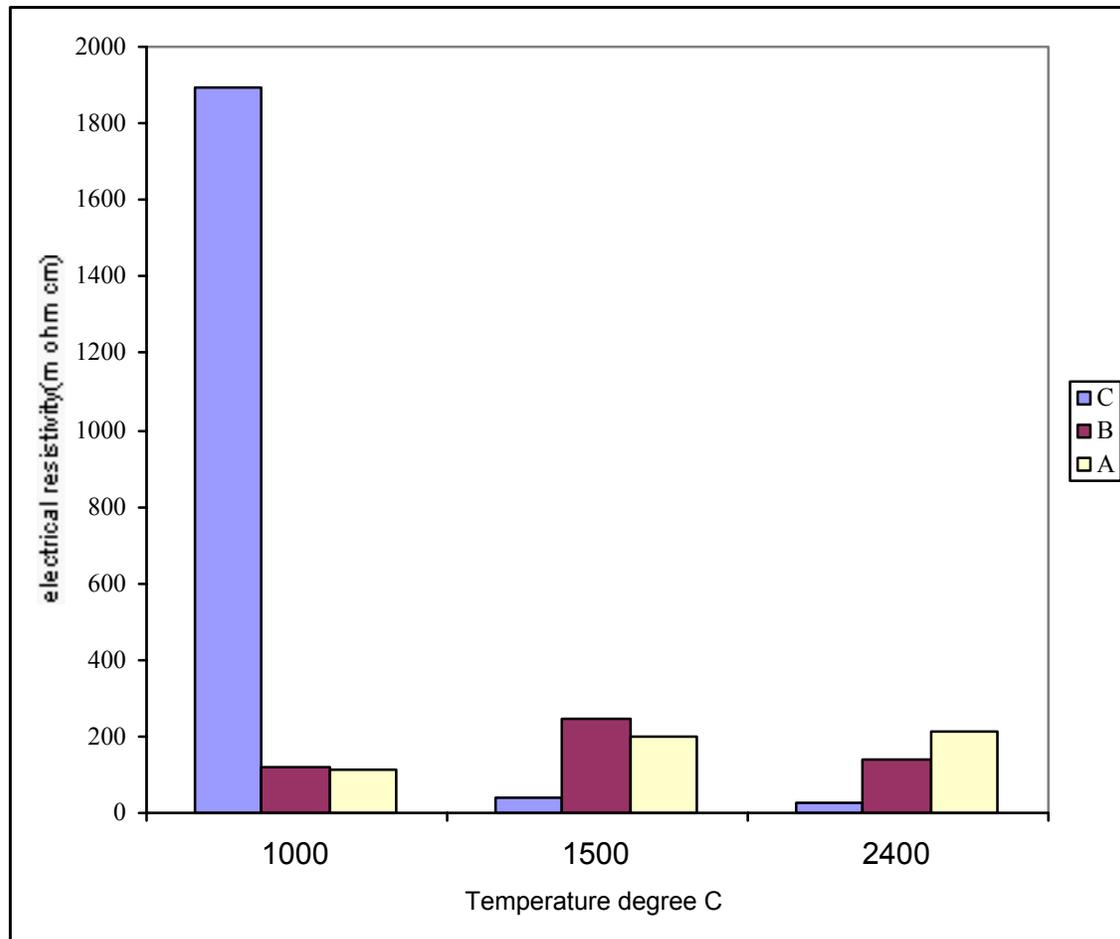
Figure 3. Changes in electrical resistivity of composites A, B and C with heat treatment temperature

Conclusion

- Density alone in carbon-carbon composites can not be taken as a sole criteria for obtaining high thermal conductivity with VGCF as reinforcement.

- It is rather surprising that the bonding between VGCF and pitch matrix is so strong in the absence of sufficient surface functionality. The study needs further investigation in this direction.

-   Volume fraction of VGCF plays an important role in deciding the physical, electrical and thermal properties of C/C composites.

Acknowlegements

REFERENCES

1. Carmona F., Physica A 1989;157 (461) .
2. Lux F., J. Mater. Sci 1993; 28 (285).
3. Heremans J., Carbon 1985; 23 (431) .
4. Tahar M.Z., Dresselhaus M.S., Endo M., Carbon 1986 ;24 (67).
5. Piraux L., Nysten B., Haquenne A., Issi J.P., Dresselhaus M.S. and Endo M., Solid state communications 1984;50 (697).
6. Issi J.P. and Nysten B., Carbon fibres eds J.B.Donnet, T.K.Wang, J.C.M.Peng and S.Rebouillat, MarcelDekker, New York 1998; 27 (759).
7. Pares J.I., Matinez – Alonso A., Tascon J.M.D., Carbon 2001; 39 (1575).
8. Montes – Moran M.A., Matinez – Alonso A., Tascon J.M.D., Carbon 2001; 39 (1057).
9. MacedoF.J., Ferriera J.A., Hattum F.W.J. Van and Bernardo C.A., J.Mat. Processing technology, 1999; 92 – 93 (151) .
10. Patton R.D., Pittman Jr C.U., Wang L., Hill J.R. and Day A., Composites: part A 2002; 33 (243).
11. Brandl W., Marginean G., Chirila V., Warschewski W., Carbon 2004; 42 (5).
12. Chen Yu Mau, Ting Jyh - Ming, Carbon 2002; 40 (359).
13. Ting Jyh – Ming and Lake Max L., Carbon 1995; 33 (663).
14. Serp Ph., Figueiredo J.L., Bertrand P. and Issi J.P., Carbon, 1998; 36 (1791).
15. Mathur, R.B., O.P. Bahl, T.L. Dhami and S.K. Chauhan, Carbon Science, 2003; 4 (111-116)
16. Lavin, J.G. et.al. , Carbon 1993;31, (1001).