NEUTRON DIFFRACTION STUDIES ON SOME CARBON FIBRE REINFORCED CARBON COMPOSITES AND THEIR PRECURSOR MATERIALS

L F PAIN, P B ROSCOE
Atomic Weapons Research Establishment, M.O.D.(P.E.),
Aldermaston, Reading RG7 4PR England

1. Introduction

The properties and processing steps in making uni-directional carbon fibre re-inforced composites (CFRC) have been described previously (1,2,3).

This paper reports on some preliminary studies made to assess the uses of neutron diffraction in characterising the production method and quantifying some of the changes taking place.

Although carbon fibres on their own have been extensively studied using electron microscopy and X-ray diffraction and some agreement reached on the crystal structure (4), little structure work has been done on the CFRC system. One of the problems in doing this work by diffraction is that both the fibre and matrix material are carbon and have similar diffraction patterns. Thus the addition of a matrix material during the processing stage mainly alters the absolute intensity of the diffraction peaks and only produces very subtle changes in the profile. In order therefore, to measure quantitatively the changes taking place during processing, it is necessary to know accurately the mass and volume of the samples in the beam. The diffraction scans, normalised to volume or mass, can then be subtracted to quantify the differences.

Neutron diffraction has some advantages over X-rays in this respect. Apart from having an isotropic form factor there are no polarization or Compton scattering effects. Thus there are fewer corrections to make to the data. However one of the most important advantages for this work is the very low absorption of neutrons. The neutron linear absorption co-efficient (μ) for carbon is 0.0005 compared with 1.3 for X-rays. This makes it possible to measure the bulk properties of large samples for which it is easy to measure accurately the mass and volume.

2. Experimental

The neutron diffraction work was done on the HERALD 5 MW reactor at AWRE using monochromatic 0.11 nm (1.1 Å) neutrons.

CFRC materials using both High Strength (HT) (Surface treated - S) and HT (untreated - U) fibres were investigated (i) at the cured resin (green) stage, (ii) after carbonising in an inert gas and (iii) after the chemical vapour densification (CVD) process. In addition studies were made on matrix materials on their own.

Large samples 8x8x40 mm were used so that the weight and volume in the neutron beam could be accurately measured.

As the carbon in the samples is oriented at least two measurements were required on each sample, one looking for carbon with its layer planes parallel to the fibre axis and one looking for the layer planes lying perpendicular to the axis.

3. Results and discussion

The diffraction patterns produced by the step scan diffractometer were typical for those of a turbostratic poorly graphitised carbon. From these diffraction scans, done at different production stages, we calculated or made deductions on:-

(1) The build up of carbon (i) with layer planes parallel to the fibre axis and (ii) perpendicular to the fibre axis. These results were calculated from the integrated intensity of the diffraction peaks.

(2) Spacing of the (001) and (hk) planes.

(3) Mean crystallite size and elastic strain

(4) Distribution of (002) plane spacing (interlayer distances)

(5) Concentrations of small defects, from diffuse background measurements.

The results obtained do of course represent the mean value for the whole sample.

3.1 HTU system

Table 1 shows the way the carbon built up during processing. It should be noticed that the CVD process also produced carbon with its layer planes oriented perpendicular to the fibre axis.

Further investigation of the CVD process showed that a low temperature xylene source gas did not lay down carbon oriented perpendicular to the fibre carbon layers, but a higher temperature CVD process did.

Although the spacings of the layer planes calculated from the peaks showed little difference during processing, there were changes in peak profile. All the (001) peaks were asymmetric in shape and showed that the interlayer spacing varied significantly about the turbostratic value, probably with a continuous variation.

From this initial study only a simple analysis of the mean crystallite size and elastic strain was undertaken and the results are of most use in comparing changes taking place.

Using Fourdeux's concept of crystallite size (4) the mean height of the stacked layer planes (Lc) was about 2.7 nm and varied little during processing.

The strain in this direction for the HTU fibre was 1.45% rising in the green stage to 2.2%. After the carbonising and CVD process it fell to 1.56%.

The flat length of the layer plane La was about 8.6 nm and the strain in this direction 0.9%. Neither of these parameters showed much variation during processing.

These results indicate that the curing of the resin causes a considerable increase in elastic strain perpendicular to the axis of the fibre. This strain is reduced by the carbonising and CVD process, although it never falls to the original HT fibre value.

The results for the HTU glassy matrix material showed that the carbon laid down by this process had a much lower mean crystallite size than that for the CVD densifying process.

Small defects in materials are frequently one of the major factors affecting their strength. The diffuse background, that is the slowly varying background between Bragg peaks, can give information on these defects.

For the HTU green material the background was relatively high, partly due to the incoherent scattering fron the hydrogen in the resin and partly from the amorphous nature of the resin. After carbonising the background fell considerable. As C^{12} is a coherent scatterer for neutrons, the background is now mainly due to defects in the system.

After the CVD densifying process the background had halved showing that a large number of defects had been removed by this process.

Further measurements on the effect of changes of temperature of the CVD process indicated a critical temperature about 1150°C, above which the diffuse background fell even more. As this seemed to be accompanied by a fall in strength it showed that a certain number of defects may have a beneficial effect.

3.2 HTS system

It has been shown that HTU fibre gives an improved impact performance over HTS fibre in CFRC materials. However as HTU fibre become surface treated inadvertently some studies were done on CFRC materials made with HTS fibre.

The main difference noted in the HTS system was a much higher elastic strain and a lower mean crystallite size then for the HTU system. These effects are presumably due to the matrix not being able to shrink away from the fibre during carbonisation. As a result the carbon layers are much more wrinkled and strained. It is easy to detect the presence of these surface treated fibres in the carbonised materials using neutron diffraction.

4. Conclusion

The results from this study have shown that neutron diffraction can be used for the quantitative characterisation of the CFRC manufacturing process in terms of, changes in the amount of layered carbon, mean crystallite size and elastic strain. Also because of the low absorption of neutrons the measurements can be done non-destructively on actual components.

Diffuse background measurements can provide information on the very small defects in the structure, which can affect the strength. This work would be easier to do using cold neutrons of greater than 0.8 nm (8 Å) wavelengths to eliminate Bragg reflections.

Material	002 plane direction to fibre axis		
	Parallel		Perpendicular
HTU Green	-26.0	(-23.8)	None
HTU Carbonised	0	0	None
HTU CVD	13.9	(23.4)	4.6 (5.0)
HTU Glassy-matrix	21.7	(25.4)	None
HTS Carbonised	-11.6	(5.8)	None
HTU Fibre	-	-	None

Table 1: Percentage changes in integrated peak intensity during manufacture. Normalised to volume. Note: Figures in brackets allow for changes in processing volumes.

References

1. Newling D O, and Walker E J, Proc 1st International Carbon Fibres Conf, London 1971, (Paper 37).
2. Boyne L, Cook D, Hill J, and Turner K, SCI 4th London International Carbon and Graphite Conf, 1974 (Paper 128).
3. Hill J, Thomas C R and Walker E J, Proc 2nd International Conf on Carbon Fibres (Paper 19) London 1974.
4. Fourdeux A, Perret R and Ruland W, Proc 1st International Carbon Fibres Conf, London 1971 (Paper 9).