Graphite flake carbon composites with a ‘sinterable’ microbead matrix

I. Mechanical properties

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Abstract

In this paper we report a study of the effect of graphite flakes of different size and volume fraction on the mechanical properties of a fine-grained carbon produced by the ‘sinterable’ route. Mesophase microbeads have been used as a matrix and the volume percent and size of the graphite flakes have been varied. It is shown that the flakes significantly increase the work of fracture of the composite, the effect being dependent on both flake size and volume fraction. However, there is a corresponding decrease in the Young Modulus and flexural strength of the composites. The flakes are not bonded to the structure and effectively act as inherent ‘crack-like’ pores. Flakes aligned perpendicular to the surface form the flaws that control the fracture stress. However, they also contribute significantly to the bridging stresses in the wake of the crack, so enhancing the work of fracture. The results should be useful in understanding the role of graphite-flake inclusions in modifying the properties of carbon materials.

Keywords: A. Carbon composites; Graphite; Carbon microbeads; D. Mechanical properties

1. Introduction

The widespread application of fine-grained monolithic carbon is often limited by brittle mechanical behaviour, flaw sensitivity, and variability in properties [1,2]. The strength values of most commercial fine-grained graphites usually lie in the range of 20–100 MPa. These materials vary in microstructure depending upon the characteristics of the particles, which are usually of coke type origin. In some cases, however, natural flake graphites are incorporated into the structure. These increase thermal conductivity and modify friction and wear properties. However, there is no firm evidence of the role played by such flakes in controlling the fracture behaviour of the carbon body. It is well known that an important factor contributing to the fracture toughness of polygranular carbon materials is the lamellar domain type of microstructure and the presence of disclinations within this structure [1].

Significant improvement in the flexural strength of fine-grained carbon (up to 200 MPa) can be achieved by the so-called 'sintering' process, in which mesophase powders are compacted and directly heated to form a carbon body of high bulk density [3–6]. These materials, although strong, are even more prone to catastrophic failure and strength variation than the traditional forms. Mechanisms for improving the toughness, without drastically changing the cost, are thus required. One possible method of increasing the toughness and hence the reliability and thermal shock resistance of brittle materials is to incorporate weak interfaces into the material which act to deflect propagating cracks and promote crack bridging [7]. Natural flake graphite is a possible agent that could impart this characteristic behaviour to a brittle carbon matrix. A weak interface may arise from two effects. The low energy basal
Table 1
Some physical properties of the raw materials used in this work (calculated relative to the original volume of KMFC powder). The powders were mixed together in the dry state and then passed through a 500-μm sieve for a better homogenisation. The sieved powders were pressed in a steel die under 140 MPa. The pellets were heat-treated slowly under an argon atmosphere up to 1500 °C. A flow diagram of the preparation procedure is shown in Fig. 1. The processing parameters are based on previous studies of KMFC [3].

<table>
<thead>
<tr>
<th>Constituent</th>
<th>Density (g cm(^{-3}))</th>
<th>Particle size (μm)</th>
<th>Purity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mesophase microbeads</td>
<td>1.42</td>
<td>23</td>
<td>93.5</td>
</tr>
<tr>
<td>Fine size graphite</td>
<td>2.26</td>
<td>53</td>
<td>99.99</td>
</tr>
<tr>
<td>Medium size graphite</td>
<td>2.25</td>
<td>277</td>
<td>99.1</td>
</tr>
<tr>
<td>Large size</td>
<td>2.26</td>
<td>504</td>
<td>99.99</td>
</tr>
</tbody>
</table>

Bulk and apparent densities of the carbonised samples were measured using bar-shaped samples and employing a mercury densitometer. The true densities of finely ground samples were also measured by a helium pycnometer. Helium pycnometry was also used to measure the apparent densities of bulk samples. These are designated here as particle and apparent densities, respectively. These values were used to estimate the total (\(P_T\)), closed (\(P_C\)), and open (\(P_O\)) porosities, as well as relative density (\(\rho_r\)), using the following equations:

\[
P_T (%) = 100(\rho_p - \rho_p)/\rho_p \tag{1}
\]

\[
P_C (%) = 100(\rho_p - \rho_p)/\rho_p \tag{2}
\]

\[
P_O (%) = P_T - P_C \tag{3}
\]

\[
\rho_r = 100(\rho_p/\rho_p) \tag{4}
\]

where \(\rho_p\), \(\rho_p\), and \(\rho_p\) are true (particle), bulk and apparent densities, respectively.

Values from these measurements have been used to follow changes in open and closed porosity. However, it is recognized that there may be pores smaller than the particle size that are located within the particles and therefore inaccessible to helium. Thus, the particle densities may not precisely equal the true solid density, and

![Fabrication flow diagram for graphite flake, carbon matrix composites.](image_url)
the closed porosity values determined may be lower than the total closed porosity in the systems. Nevertheless, decisive trends resulted, as shown later.

Samples for mechanical testing were cut from the prepared disks and polished using very fine grain (1 μm) polishing papers, to eliminate surface flaws that may control the fracture stress. The final dimensions of the samples were approximately 25×3×3 mm. Testing was performed on a Mayes instrument at a ram speed of 0.5 mm/min. Flexural strength and modulus were measured at room temperature by three-point bending with a 20-mm span. The flexural modulus of the composites was calculated from the slope of the tangent to the initial straight-line portion of the load–deflection curves.

Four samples for each composite were measured for each of the properties identified above. X-ray pole figures were used to identify the orientation of the graphite flakes. The (0002) plane was used for the tracing of the flake orientation.

3. Results and discussion

3.1. Density

Fig. 2 shows the density results for all three series of composites. Irrespective of the type, the bulk density was the same for samples with the same vol.% of flakes, but decreased slightly for each graphite flake size as the graphite content increased. The true, or particle, densities of the composites rose as the vol.% of the flakes increased. This was also independent of flake size and is a result of the higher density of the flakes. The fact that the bulk densities decrease with vol.% of graphite means that the porosity increases and the total porosity is the same at each vol.% of graphite regardless of flake size (Fig. 3). However, Fig. 2 also shows that whilst the apparent densities of the medium (mCC) and large (lCC) flake composites are the same at each graphite content, those for the fine graphite composites (fCC) are significantly higher, showing that the latter have lower closed porosities.

The open, closed, and total porosities are shown for the fine graphitic composites in Fig. 3 and for medium and large ones in Fig. 4. It can be seen that the closed porosity
decreases with increasing graphite content for the fine series, but is almost constant for the other two. At 15 vol.% graphite, the open porosity in the fCC material is ~50% higher than that in the mCC and lCC. This difference can be explained by the difference between the sizes of the flakes. At the same volume fraction, the number and surface area of the fine flakes are higher than those of the medium and large flakes. Also, the interconnectivity of the graphite flakes will be higher in the fCC than in the mCC and lCC. Due to the thermal expansion mismatch between the flakes (c-axis) and the matrix, each flake is associated with a lamellar crack. Therefore interconnected channels (open porosity) are more likely to be present in the fCC, than in the mCC and lCC. Fig. 5a–c shows micrographs of the composites at 10 vol.% graphite demonstrating typical features. The KMFC matrix, itself, is in fact, a composite with an isotropic ‘binder’ phase, within which is dispersed anisotropic spheres, derived from the second phase, the mesophase. The closed porosity resides within the KMFC matrix phase. The regions of coherent matrix phase are smaller in size in the fCC than in mCC and lCC at the same graphite volume content. So the closed pores are more likely to be present in the latter two, as shown in Figs. 3 and 4.

Fig. 5 shows also that the graphite flakes have a preferred orientation, tending to align with their c-axes parallel to the pressing axis of the composite. In order to follow the effect of graphite size and volume content on the orientation of the flakes, (0002) peak pole figures were obtained from the polished surface of the samples (perpendicular to the pressing axis). Typical pole figures of the fabricated samples are shown in Fig. 6 for fine and large size flake composites. These pole figures showed that increasing the volume content of fine flake graphite in the composite does not change the orientation of the flakes considerably. In the 5 vol.% fCC most of the flakes are oriented with their c-axes within 30° of the pressing axis (i.e., the basal planes are approximately parallel to the surface of the specimen). This angle rises slightly to about 40° at 15 vol.%. However, in both cases, there is a small number of flakes with their c-axes oriented at about 80° to the pressing axis (thick curves pointed by arrows in Fig. 6a,b), which is close to a vertical alignment of the flakes to the surface of the composites. This nearly vertical alignment of the flakes, shown also in the micrograph in Fig. 7, can be the origin of flaws, as will be shown later.

For the 5 vol.% large size flake composite there is again a very good alignment of the flakes, as can be seen from the central pattern in Fig. 6c. This figure shows that the majority of the large flakes are aligned nearly parallel to the surface of the composite, with a deviation of less than 10°. For 15 vol.% large flake composite, there is less alignment (Fig. 6d). Yet, again there are traces of nearly vertical alignment of the flakes for both the 5 and 15 vol.% of the large flake composites (thick curves pointed by arrows in Fig. 6c,d). The intensity ratios of the lines in

Figs. 6–d indicates that the extent of nearly vertical alignment of the flakes relative to the surface of the composites for fine size flake composites (i.e., parallel to
Fig. 6. (0002) Pole figures of graphite in composites: (a) 5 vol.% fine graphite, and (b) 15 vol.% fine graphite; (c) 5 vol.% large graphite, and (d) 15 vol.% large graphite.

the pressing direction) is roughly four times that of the large flake composites (0.5/2 for large and 1/1 for fine composites).

3.2. Mechanical properties

Incorporation of natural graphite flakes in the
mesophase-based matrix is accompanied by a progressive decrease in both flexural strength and modulus with increasing graphite size and content (Figs. 8 and 9). The flexural modulus decreases almost linearly with graphite vol.% However, the flexural strength falls initially, from 0 to 5 vol.%, but then changes only slightly. Measurements were made with two different flake orientations, defined in Fig. 10. The flexural modulus ($E$) and flexural strength ($σ$)
are designated $\sigma_{t}$, $E_{t}$, $\sigma_{s}$ and $E_{s}$ when the load is applied perpendicular and parallel to the pressing axis, respectively. As can be seen, both $\sigma_{s}$ and $E_{s}$ are slightly smaller than $\sigma_{t}$ and $E_{t}$. Load–displacement curves (Fig. 11) show dramatic changes in fracture mechanism, from catastrophic for the matrix to a more graceful (controlled) type of crack propagation for the composites. This behaviour is different for fine and coarse graphite contents.

The apparent work of fracture (w.o.f) was estimated from the areas under the curves for the composites, which were not notched (Fig. 12). The measured values for the matrix may therefore be inaccurate, since the fracture was not controlled, but for the composites the values are probably fairly accurate, since the flakes are acting as notches and the fracture is a more stable process. Full details of the notch sensitivity of these materials will be discussed elsewhere. However, the results are significant enough to follow the effects of the flakes on the work of fracture, which increases significantly with graphite vol.%. For ICC and mCC the w.o.f increases sharply to 5 vol.%, which then stabilizes for these composites. For the fine ones, however, the w.o.f increases gradually. Both w.o.f and load–displacement results show that although the addition of graphite decreases $\sigma$ and $E$ values, it has a very significant effect on increasing the toughness, producing a highly damage-tolerant material. The work of fracture increases almost 10 times for the ICC. It is interesting to compare the w.o.f values with those of typical ceramics. The w.o.f of the matrix itself is higher than typical values for brittle ceramics. Incorporation of the graphite increases it even further.

The decrease in $E_{t}$ and $E_{s}$ is probably due to the increase in porosity. However, the large flakes reduce $E$ more effectively than do the fines, because of the aspect ratio of the crack associated with the flake. This probably also accounts for the difference in $E$ values for the two different orientations. An empirical expression that relates $E$ to porosity ($p$) is [8]:

$$E = E_{o} \exp(-ap)$$

(5)

where ‘$E_{o}$’ and ‘$a$’ are constants. It has been shown that ‘$a$’ is a function of crack dimension, being greater for lamellar cracks [8]. This equation can fit the data, giving values of ‘$a$’ which increase with graphite flake size. The ‘$a$’ values are large, but lower than those observed by Button and Rand [9] for graphite–alumina composite refractories. They are consistent with cracks of high aspect ratio [8].

The KMFC matrix is a brittle carbon and flaws control its strength. The introduction of the graphite flakes effectively controls the size of the largest flaws in each type of composite. By incorporation of graphite, $\sigma$ initially falls, but later levels off, because there is no further increase in flaw size in this region. The interconnectivity of flaws and the ease with which they join up under stress will, of course, increase with graphite content. This would affect the Weibull modulus and this will be discussed in detail elsewhere. Fig. 7 shows the nearly perpendicular alignment of some of the flakes relative to the surface, which must be considered as the origin of the fracture-controlling flaws. This consideration applies to both orientations of testing.

The increase in the work of fracture and the changes in the load–displacement curves clearly show the toughening effect. Fig. 13 shows the crack pattern in a typical
Fractured specimen, demonstrating that a number of well known mechanisms for increasing the toughness of brittle materials are in operation. These are:

- crack deflection around intact flakes;
- crack bridging by flakes;
- flake pull-out effects;
- flake rupture has also been observed.

A more detailed study of fracture behaviour will be reported later.

The strengths of the fCCs with the same amount of porosity are higher than those of the mCCs and lCCs. This could be accounted for by the difference between the sizes of the misaligned lamellar cracks in the composites. According to Griffith’s equation, strength is proportional to $c^{-1/2}$ in which $c$ is the flaw size in a material (including cracks and pores). Therefore, the larger the defect size, the lower should be the strength. The small difference in strengths when measured in the different directions would therefore seem to be a result merely of the difference in the flexural moduli. However, this is speculative at this stage and a spatial statistical approach to the characterisation of the microstructure and flake orientations in the bulk of the composites is required for a definitive answer.

The graphite flakes can be regarded as cracks, which are intentionally incorporated into the composites and function as strength-controlling agents. Thus, it is possible to predict the fracture strengths using the Griffith approach, as will be shown elsewhere. Since the most severe flaws are now controlled by the flakes, the strength variation from sample to sample is considerably reduced, as indicated by a significantly increased Weibull modulus [10,11], as will also be discussed in greater detail elsewhere.

In order to describe the properties of these composites, different curve-fitting regression analyses have been used. One of the most promising for fCC composites is (Fig. 14):

**Fig. 8.** Effect of (a) volume content and (b) graphite size on the flexural strength of graphite carbon composites measured in different orientations.

**Fig. 9.** Effect of (a) volume content and (b) graphite size on the flexural modulus of graphite carbon composites, measured in different orientations.
Fig. 10. Diagram showing the direction of mechanical testing of the samples for the results shown in Figs. 8 and 9.

\[
\sigma = 144.17 \exp(-0.0469V) \quad R^2 = 0.9244
\]

(6)

where \( \sigma \) is the flexural strength, and \( V \) is the volume content of graphite, which is in the form of Eq. (5), i.e.,

\[
\sigma = \sigma_e \exp(-ap)
\]

(7)

where \( \sigma_e \) is the theoretical strength, \( a \) is the constant, and \( p \) is the pore (graphite) fraction. It can be seen that \( \sigma_e \) is 144.17 MPa, which is close to the strength of the KMFC matrix (148 MPa) and this analysis illustrates that the graphite volume content can be considered as a pore fraction in the composite. However, Eq. (5) is not the best curve fit equation regarding \( R^2 \). The following empirical polynomial seems to provide the best fit so far

\[
\sigma = 148 - 7.742V + 0.444V^2 - 0.01V^3 \quad R^2 = 1
\]

(8)

Similar trends have been observed for larger size graphite and also for the variation of the strength of the composites with graphite flake size. According to these studies a

Fig. 11. Typical load–deflection diagrams for un-notched samples, matrix carbon, fine and large flake composites (15 vol.%).
third-order polynomial seems to be the best for description of the strengths of these materials.

4. Conclusion

Graphite flake-containing carbon composites (GFCC) are a new kind of CC in which the incorporation of graphite has the effect of decreasing strength and elastic modulus (E) whilst increasing significantly the work of fracture. Hence, higher thermal shock resistance is expected for these composites. The graphite flakes act like relatively ordered cracks of a certain size and thereby control the composite strengths.

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Fig. 14. A typical curve fitting for flexural strength of the fine flake composites.

References


