POSTER

FABRICATION OF FINE GRAINED CARBON/GRAPHITE FROM MESOPHASE MICROBEADS

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Introduction

Fine grained carbon materials of high strength can be produced from mesophase microbeads [1-3] by a "sintering" operation. Fuduka et al.,[1] have described the production of microbeads from coal tar pitch (Kawasaki Mesophase Fine Carbon, KMFC) which are available commercially and are reported to yield strength as high as 150 MPa. An important aspect of fabrication is the control of the densification and the avoidance of bloating phenomena in the compacted powder during heat treatment. This is governed by the softening properties of benzene-insoluble, quinoline-soluble compounds (β-resin) in the materials [1].

Experimental

The chemical analysis and the physical characterisation of the KMFC powder used in this study are summarised in Table 1.

Table 1: Chemical analysis and physical characterisation of green KMFC powder.

Chemical analysis:	
Toluene insoluble/ wt%	98
Quinoline insoluble/ wt%	90.2
Volatile matter/ wt%	9.3
Ash/ wt%	0.22
Physical Characterisation:	
Mean particle size/ μm	11
Binder phase (in-situ)/vol%	~37
Powder density/ g cm^{-3}	1.42

KMFC pellets were formed by uniaxially pressing to 10 MPa followed by cold isostatic pressing (CIP) to various pressures ranging from 50 to 400 MPa. These formed pellets were heat treated to 900 °C with different heating rates in an inert high purity Ar atmosphere.

KMFC pellets CIP to 200 MPa were heat treated to different temperatures from 200 °C to 2000 °C to study the changes in their microstructures and properties with temperatures. Heating rates used for heat treatments were 10 °C hr^{-1} for temperatures ≤900 °C, 180 °C hr^{-1} for temperatures ≥900 °C to ≤1500 °C and 600 °C hr^{-1} for temperatures ≥ 1500 °C.

Where materials are to be heat treated to high temperatures, it may be commercially expedient to adopt a two stage process in which the initial carbonised materials is further heat treated. To examine whether this cooling-reheating schedule results in changes to the microstructure, materials so produced were compared with similar ones processed to the same final temperature without intermediate cooling. KMFC pellets CIP to 200 MPa were heat treated to 1500 °C using two heat treatment schemes as shown below. The results of this study are shown in Table 2.

Scheme 1:

$$RT \xrightarrow{10°C/hr} 800°C(2hr) \xrightarrow{200°C/hr} RT$$

$$\xrightarrow{180°C/hr} 1500°C(2hr) \xrightarrow{200°C/hr} RT$$

Scheme 2:

$$RT \xrightarrow{10°C/hr} 800°C(0hr) \xrightarrow{180°C/hr} 1500°C(2hr)$$

$$\xrightarrow{200°C/hr} RT$$

Results and Discussion

Effects of forming pressure and heating rate

Increasing the forming pressure resulted in an increase in the bulk density and reduction in pore volume of the green KMFC compacts as shown in Figure 1. As a result of the decrease in pore volume, the range of heating rates that can be applied during heat treatment without causing bloating are largely reduced with increasing forming pressure, as shown in Figure 2(a). At heating rates lower than that which initiated bloating, increasing the rates usually resulted in compacts with higher bulk densities. The retention of volatile matter reduced the viscosity of the liquid phase when part of the material underwent liquid phase carbonisation[1]. This trend can be seen very clearly in the 50 MPa formed KMFC (Figure 2(a)). Higher forming pressures usually resulted in heat treated samples with higher bulk densities(Figure 2(a)). However, the trends are reversed in apparent densities as shown in Figure 2(b). This is thought to be caused by the adverse effects of retention of volatile matter on the structure of the carbon. These low molecular weight fractions are believed to be highly reactive and have a tendency to cross-link in the liquid phase and hence hinder the aromatic molecules from aligning into more ordered lamellae structures required for precursors of graphitic carbon [4]. Increases in forming pressure and heating rates have similar effects in delaying the escape of the volatile matters; hence they would both increase bulk density and decrease apparent density.

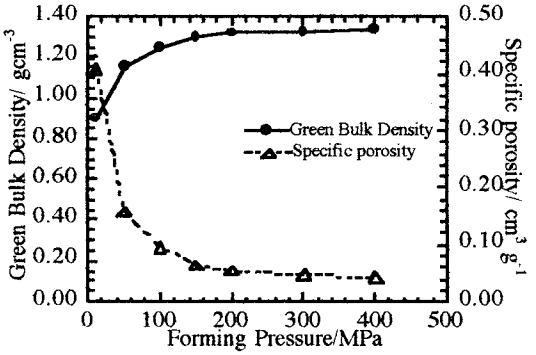

Figure 1 : Bulk density and specific porosity of green KMFC compact vs. forming pressures.

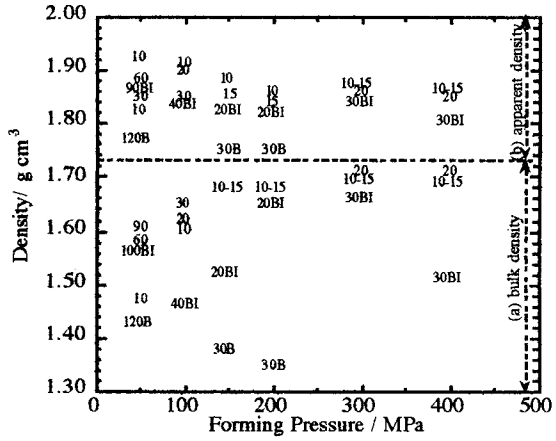

Figure 2: Effects of forming pressure and heating rate on (a) bulk density and (b) apparent density of 900 °C heat treated KMFC. Numbers on the co-ordinates are the heating rates in, °C/hr, which result in the corresponding bulk and apparent densities on the y-axis, in (a) and (b) respectively, for samples formed with corresponding pressures on the x-axis. BI indicates initiation of bloating, B indicates sample bloated.

Effects of heating and cooling

KMFC experienced a 10 % weight loss and 40 % volume shrinkage when heat treated to 2000 °C at which a bulk density of 1.92 g cm^{-3} and helium density of 2.05 g cm^{-3} were obtained, as shown in Figure 3. The apparent porosity reached a maximum of 14 vol % at 800 °C before reducing to 5 to 6 vol % at T ≥1300 °C. The significant reduction of the apparent porosity between 800 °C and 1300 °C was not expected as heat treatment at these temperatures involved solid state processes which gave rise to densification of individual constituent materials but should not eliminate inherent pores. These peculiar results might be explained by the results from the study of effects of cooling on densification as shown in Table 2. It was found that having been cooled to room temperature from 800 °C, the samples which were heat treated using Scheme 1 have lower bulk density and higher porosity than samples heat treated directly to 1500 °C using Scheme 2. Microstructures show that Scheme 1 sample has many multiple cracked mesophase spheres which are not common in the Scheme 2 sample. Samples produced at temperatures in the range of 600-900 °C may also generate cracks which contribute to the high pore volumes.

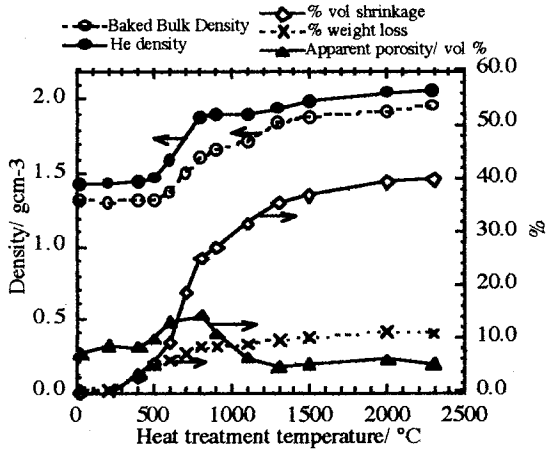

Figure 3: Changes of KMFC compacts with respect to heat treatment temperatures.

Table 3. Different physical characteristics of 'Scheme 1' and 'Scheme 2' 1500 °C heat treated KMFC pellets.

Sample	Bulk density /g cm^{-3}	Helium density /g cm^{-3}	Apparent porosity/vol. %
'Scheme 1'	1.82	1.99	8.5
'Scheme 2'	1.88	1.99	5.5

Conclusion

Sintering behaviour of mesophase microbeads is a complicated subject. Slight changes in the processing parameters will not only alter the microstructures but will also affect the structures of the carbon materials on the molecular scale. These will in turn affect both their mechanical and physical properties

References

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