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Effect of calcination conditions of self-sintering mesocarbon microbeads on the characteristics of resulting graphite

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Mesocarbon microbeads are now-a-days used as a prominent self-sintering precursor for the production of high density monolithic graphite. The quality of this graphite is highly dependent on the characteristics of these microbeads, such as the quinoline and toluene insoluble contents, β-resins content and volatile matter content, which in turn, can be controlled to desired values by suitable treatments of their extraction and calcination. In the present paper, the authors give an account of the study conducted to see the effect of calcination conditions of mesocarbon microbeads on the characteristics of the resulting graphite. A calcination at a temperature in the range of 280–320 °C for 30 min. under an ambient pressure of nitrogen, or at a temperature of 245–310 °C for 10 min. under a reduced pressure (5 cm Hg) of nitrogen, results in mesocarbon microbeads having a quinoline insoluble content of 83.6–89.8%, toluene insoluble content of 94.4–99.7%, β-resins content of 6.8–11.9% and a volatile matter content of 10.2–13.5%. Such microbeads have been found to lead to a monolithic graphite possessing a bulk density 1.91–2.02 g cm^{-3}, bending strength of 62–70 MPa, Shore hardness of 58–69, electrical resistivity of 2.1–2.6 mΩ cm and a degree of anisotropy of 1.02–1.05.

1. Introduction

Mesocarbon microbeads (MCMB) are now well-established as a raw material, requiring no external binder, for the production of dense and strong monolithic graphite [1–4]. As these microbeads act as a self-sintering material, the characteristics of this type of graphite depend, besides other factors, on the characteristics of these microbeads, namely, the quinoline and toluene insoluble contents, β-resins content, and volatile matter content, which in turn, can be controlled to desired values to a large extent by controlling the conditions of their extraction. However, in addition to extraction, another important step in the overall process of production of MCMB-based high density monolithic graphite is the calcination of the MCMB under suitable conditions. The main purpose of this calcination is to remove any residues of the solvent (used during solvent-extraction) entrapped in the mesocarbon microbeads. Another objective is to adjust the amount of binding components adhering to the microbeads. Though a number of papers have appeared in the literature on the development of this MCMB-based specialty graphite [5–9], no information is available on the effect of calcination conditions of the microbeads on the characteristics of the resulting graphite. In view of this, the present authors have conducted a study on this aspect during the development of this specialty graphite [10–15]. In this study, a systematic preparation was carried out to see the effect of calcination conditions of mesocarbon microbeads, namely, time, temperature and atmosphere (inert/vacuum) of calcination, on the characteristics of the resulting high density graphite. The study was carried out in two parts. In the first part, the calcination was done under an ambient pressure of nitrogen (inert atmosphere) and in the second part, the calcination was carried out under a reduced pressure of nitrogen. The present paper gives a complete account of the work done by the authors in this direction.

2. Experimental procedure

A coal tar pitch with quinoline insolubles (QI) content of 2.6% with its other characteristics given in Table I was heat-treated at a temperature of 425 °C in an atmosphere of nitrogen for 2.5 h in two separate batches to generate the mesophase spherules. The properties of the heat-treated pitches (Mesophase Pitch - I and Mesophase Pitch - II) are also given in Table I. The optical micrographs of the mesophase pitches are shown in Figs 1 and 2, while the graphs of differential and cumulative frequencies of the mesophase spherules as a function of their size obtained in the two cases are shown in Figs 3 and 4. The mesophase pitches were then extracted with a Tar oil boiling in the temperature range of 230–270 °C to obtain two lots of mesocarbon microbeads, designated as MCMB-I and MCMB-II. Parts

TABLE I Characteristics of precursor coal tar pitch and mesophase pitches - I and II

S. No.	CHARACTERISTICS	COAL TAR PITCH	MESOPHASE PITCH-I	MESOPHASE PITCH-II
1.	Softening point (°C)	76	—	—
2.	Quinoline insoluble content (%)	2.6	25.3	26.6
3.	Toluene insoluble content (%)	21.7	59.3	60.2
4.	β-resins content (%)	19.1	34.0	33.6
5.	Coking yield (%)	47.6	71.1	71.6
6.	Ash content (%)	0.06	—	—
7.	Specific gravity	1.28	1.30	1.29
8.	Size of mesophase spherules			
	a) Predominant range (μm)		4–16	4–16
	b) Median (μm)		7.4	8.6
	c) Mean (μm)		9.4	9.8

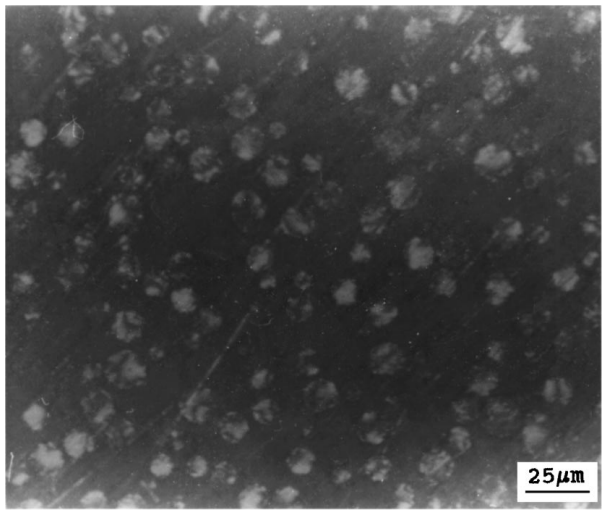

Figure 1 Optical micrograph of Mesophase Pitch I.

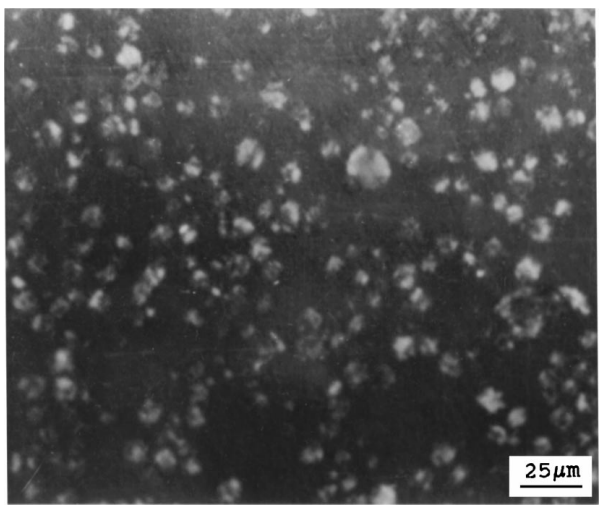

Figure 2 Optical micrograph of Mesophase Pitch II.

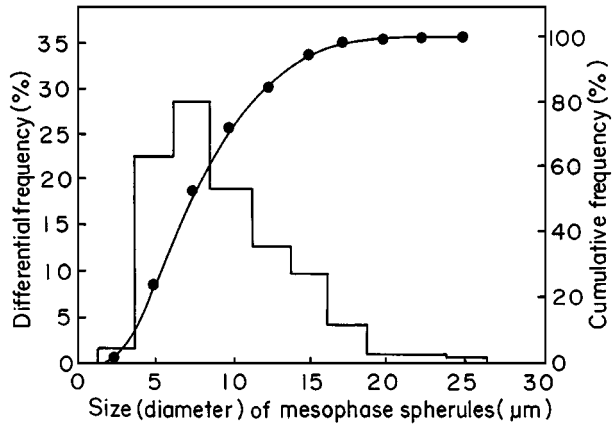

Figure 3 Differential and cumulative frequencies of mesophase spherules formed in Mesophase Pitch I as a function of their size.

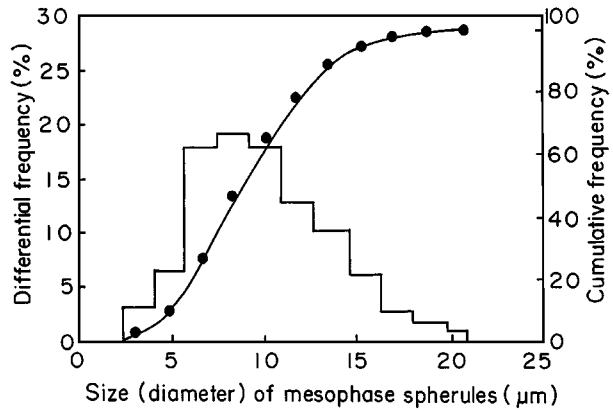

Figure 4 Differential and cumulative frequencies of mesophase spherules formed in Mesophase Pitch II as a function of their size.

of MCMB-I were then calcined in separate batches at temperatures of 240, 280 and 320 °C for a period of 30 min. each in an inert atmosphere of nitrogen to obtain three batches of the calcined MCMB-I, called as IA, IB and IC, respectively. In a similar way, the MCMB-II was calcined in separate parts at temperatures of 215, 230, 245, 260, 285 and 310 °C under a reduced pressure of nitrogen (5 cm Hg) for 10 min. each to obtain six different batches, designated as IIA, IIB, IIC, IID, IIE and IIF, respectively. All these batches of microbeads were then characterised with respect to quinoline and toluene insoluble contents, β-resins content and volatile matter content. The calcination conditions and the characteristics of the calcined MCMB-I and MCMB-II are given in Tables II and III, respectively.

The microbeads of all the batches of MCMB-I and MCMB-II, calcined as well as uncalcined, were then hot-moulded into small rectangular plates of size 60 mm × 20 mm × 4 mm using a conventional hydraulic press. The plates obtained were carbonised to a temperature of 1100 °C, half of which were graphitised also to 2700 °C. Finally, the resulting carbonised and

graphitised plates from MCMB-I and MCMB-II were tested with respect to various characteristics, the values of which are compiled in Tables IV–VIII. In addition, specimens of the plates of both these materials were also subjected to optical microscopy and some of the micrographs are shown in Figs 5 and 6.

TABLE II Characteristics of mesocarbon microbeads - I (MCMB-I) calcined at different temperatures under ambient pressure of nitrogen

S. No.	CHARACTERISTICS	BATCH I	IA	IB	IC
1.	Calcination parameters:				
	(i) Temperature (°C)	—	240	280	320
	(ii) Residence time (min.)	—	30	30	30
	(iii) Yield (%)	—	92.5	91.5	91.0
2.	Quinoline insoluble content (%)	74.9	81.3	85.9	89.0
3.	Toluene insoluble content (%)	93.6	97.7	97.8	99.7
4.	β-resins content (%)	18.7	16.4	11.9	10.7
5.	Volatile matter (%)	15.4	11.4	11.1	10.8

TABLE III Characteristics of carbon plates based on mesocarbon microbeads-I calcined at different temperatures under ambient pressure of nitrogen (HTT = 1100 °C)

S. No.	CHARACTERISTICS	BATCH I	IA	IB	IC
1.	Green density (g/cm^3)	1.30	1.28	1.29	1.28
2.	Baked density (g/cm^3)	1.69	1.69	1.69	1.70
3.	Weight loss (%)	15.6	11.4	11.0	10.1
4.	Volume shrinkage (%)	32.0	32.5	31.5	34.0
5.	Linear shrinkage (%)	13.4	12.8	12.2	11.9
6.	Bending strength (MPa)	23	50	87	85
7.	Shore hardness	40	58	82	85
8.	Electrical resistivity (mΩ cm)	—	5.8	4.7	4.9

TABLE IV Characteristics of graphitised plates (HTT = 2700 °C) based on mesocarbon microbeads-I calcined at different temperatures in an atmosphere of nitrogen

S. No.	CHARACTERISTICS	BATCH I	IA	IB	IC
1.	Green density (g/cm^3)	1.30	1.28	1.29	1.28
2.	Graphitised density (g/cm^3)	1.86	1.93	1.96	1.97
3.	Weight loss (%)	20.6	16.6	16.3	16.0
4.	Volume shrinkage (%)	43.2	44.2	44.6	45.9
5.	Linear shrinkage (%)	18.0	18.2	18.6	19.0
6.	Bending strength (MPa)	—	56	69	70
7.	Shore hardness	—	63	68	69
8.	Coeff. of thermal expansion ($\times 10^{-6}$/K)	—	6.5	6.7	6.8
9.	Degree of anisotropy	—	1.04	1.03	1.05
10.	Electrical resistivity (mΩ cm)	—	2.6	2.5	2.6

TABLE VI Characteristics of carbon plates (HTT=1100°C) based on mesocarbon microbeads-II calcined at different temperatures under reduced pressure of nitrogen

S. No.	CHARACTERISTICS	BATCH II	IIA	IIB	IIC	IID	IIE	IIF
1.	Green density (g/cm^3)	1.36	1.34	1.32	1.32	1.31	1.31	1.28
2.	Baked density (g/cm^3)	1.80	1.78	1.74	1.72	1.72	1.72	1.71
3.	Weight loss (%)	16.1	15.9	15.4	13.3	13.5	14.4	13.8
4.	Volume shrinkage (%)	36.9	36.8	36.1	34.2	33.6	33.7	35.6
5.	Linear shrinkage (%)	14.1	13.8	13.5	13.0	12.6	12.7	13.7
6.	Bending strength (MPa)	17	28	45	78	81	84	79
7.	Shore hardness	—	—	58	56	64	68	75
8.	Electrical resistivity (mΩ cm)	5.8	5.4	5.3	4.4	5.1	4.1	4.0

3. Results and discussion

3.1. Mesophase formation

It is clear from Figs 1–4 that in both the cases, the heat-treatment of the precursor coal tar pitch at 425 °C for 2.5 h results in the formation of mesophase spherules with their predominant size lying in the range of about 4–16 μm (see also Table I). It is further seen from Table I that the heat-treatment results in the increased values of quinoline and toluene insoluble contents and the coking value of the resultant mesophase pitches, which is obviously due to the removal of volatile constituents as well as to the condensation and polymerisation reactions among the various molecular species.

3.2. Part-I: Calcination of mesocarbon microbeads under nitrogen atmosphere

It is seen from Table II that the quinoline insoluble content of the microbeads increases from the initial value of 74.9% to values of 81.3, 85.9 and 89.0% as the calcination temperature increases from 240 to 280 °C and then to 320 °C, and the toluene insoluble content increases from the initial value of 93.6% to values of 97.7, 97.8 and 99.7% at these temperatures, respectively. The volatile matter content, in turn, decreases from the initial value of 15.4% to values of 11.4, 11.1 and 10.8% at these respective temperatures. These variations in the characteristics of the microbeads are due to the removal (evaporation) of entrapped tar oil components and other low molecular weight species from the microbeads, as well as due to the polymerisation and condensation reactions among the various aromatic molecules adhering to the microbeads.

Regarding the characteristics of carbon plates based on MCMB-I, it is seen from Table III that both the green

TABLE V Characteristics of mesocarbon microbeads-II (MCMB-II) calcined at different temperatures under reduced pressure of nitrogen

S. No.	CHARACTERISTICS	BATCH II	IIA	IIB	IIC	IID	IIE	IIF
1.	Calcination Conditions:							
	(i) Temperature (°C)	—	215	230	245	260	285	310
	(ii) Residence time (min.)	—	10	10	10	10	10	10
2.	Quinoline insoluble content (%)	75.2	78.0	82.2	83.6	84.3	86.2	89.8
3.	Toluene insoluble content (%)	91.5	92.6	93.7	94.4	94.9	96.4	96.6
4.	β-resins content (%)	16.3	14.6	11.5	10.8	10.6	10.2	6.8
5.	Volatile matter content (%)	15.2	14.0	13.7	13.5	13.0	12.0	10.2

TABLE VII Data showing correlation of apparent baked and green densities in terms of weight loss and volume shrinkage

BATCH	CALCINATION TEMPERATURE (°C)	APPARENT GREEN DENSITY (GD) (g/cm^3)	FRACTIONAL RESIDUAL WEIGHT (a)	FRACTIONAL RESIDUAL VOLUME (b)	DENSITY AMPL. FACTOR ($c = a/b$)	EXPECTED BAKED DENSITY (GD°C) (g/cm^3)	ACTUAL BAKED DENSITY (g/cm^3)
II	—	1.36	0.839	0.631	1.330	1.81	1.80
II-A	215	1.34	0.841	0.632	1.335	1.78	1.78
II-B	230	1.30	0.865	0.639	1.354	1.76	1.74
II-C	245	1.32	0.870	0.658	1.322	1.75	1.72
II-D	260	1.31	0.874	0.664	1.316	1.72	1.72
II-E	285	1.31	0.873	0.663	1.316	1.72	1.72
II-F	310	1.28	0.863	0.664	1.340	1.72	1.71

NOTE: Fractional residual weight (a) = 1− wt. loss (%) /100
Fractional residual volume (b) = 1− vol. shrinkage (%)/100
Density amplification factor (c) = a/b

and baked densities of the plates show almost no differences from batch to batch, with their values lying in the range of 1.28–1.30 g cm^{-3} and 1.69–1.70 g cm^{-3}, respectively. However, the bending strength of the carbon plates shows a significant improvement from 28 MPa for the uncalcined microbeads (MCMB-I) to values of 50, 87 and 85 MPa for the microbeads calcined at 240, 280 and 320 °C, respectively. These variations in the bending strength may be attributed to the differences in the characteristics of the microbeads. Further, the optical micrographs of the carbonised plates, shown in Fig. 5, reveal that the plates based on uncalcined microbeads as well as those based on microbeads calcined at 240 °C contain some cracks, whereas those made from microbeads calcined at 280 and 320 °C have no such cracks. These cracks reflect the presence of tar oil components or other low molecular weight components in the mesocarbon microbeads, which one effectively removed upon calcination at 280–320 °C.

Regarding the results of these graphitised plates, summarised in Table IV, it is found that in all the cases, the product is highly isotropic (Degree of anisotropy = 1.03–1.05). However from the point of view of a crack-free, dense and strong product, it is seen that the plates based on microbeads calcined at temperatures of 280 and 320 °C also exhibit good densities of 1.96 and 1.97 g cm^{-3} with bending strengths of 69 and 70 MPa. Besides this, these plates also show reasonably good Shore hardness values of 68 and 69 and electrical resistivities 2.5 and 2.6 mΩ cm, respectively.

From the above results, it appears that a calcination treatment of the mesocarbon microbeads (obtained as tar oil insolubles) in the temperature range of 280–320 °C in an inert atmosphere is very useful in removing the entrapped tar oil components and in reducing the contents of other low molecular weight compounds, namely, toluene solubles and β-resins to an optimum level and hence suitable for the ultimate use of the microbeads in the production of high density - high strength - isotropic graphite.

TABLE VIII Characteristics of graphitised plates (HTT = 2700 °C) based on mesocarbon microbeads-II calcined at different temperatures under reduced pressure of nitrogen

S. No.	CHARACTERISTICS	BATCH II	IIA	IIB	IIC	IID	IIE	IIF
1.	Green density (g/cm^3)	1.36	1.34	1.30	1.32	1.31	1.31	1.28
2.	Graphitised density (g/cm^3)	—	—	1.90	1.91	1.93	2.02	1.99
3.	Weight loss (%)	—	—	21.0	18.0	18.2	18.6	18.0
4.	Volume shrinkage (%)	—	—	46.0	46.3	45.0	45.6	47.0
5.	Linear shrinkage (%)	—	—	18.7	18.4	18.0	18.2	19.0
6.	Bending strength (MPa)	—	—	32	62	65	69	68
7.	Shore hardness	—	—	50	58	62	65	68
8.	Coeff. of thermal expansion ($\times 10^{-6}$/K)	—	—	—	6.4	6.6	6.9	6.8
9.	Degree of anisotropy	—	—	—	1.03	1.05	1.02	1.04
10.	Electrical resistivity (mΩ cm)	—	—	2.5	2.2	2.3	2.2	2.1

3.3. Part II: Calcination of mesocarbon microbeads under reduced pressure of nitrogen

It is seen from Table V that the calcination of MCMB-II at temperature from 215 to 310 °C results in an increase in the quinoline insoluble content from an initial volume of 75.2% (uncalcined) to values of 78.0, 82.2, 83.6, 84.3, 86.2 and 91.8% at the temperatures of 215, 230, 245, 260, 285 and 310 °C, respectively, and the toluene insoluble content from an initial value of 91.5% to values of 92.6, 93.7, 94.4, 94.9, 96.4, and 96.6% at these respective temperatures. The volatile matter content, in turn, decreases from an initial value of 15.2% to values of 14.0, 13.7, 13.5, 13.0, 12.0 and 10.2%, respectively, at these temperatures. These variations in the characteristics of MCMB-II may also be explained on the same basis as applicable to MCMB-I.

It is seen from Table VI that except for batches II and IIA, which have relatively higher baked density of 1.80 and 1.78 g cm^{-3}, respectively, the baked densities of the carbons of all the batches (IIB to IIF) lie in a narrow range of 1.71–1.74 g cm^{-3}. This behavior is in parallel with that of the green densities of these carbons, which means that the higher the green density, the higher is the baked density. In fact, it is quite reasonable also as one would see from the data shown in Table VII. The ratio of the fractional residual weight to the fractional residual volume for various batches (corresponding to different calcination temperatures) works

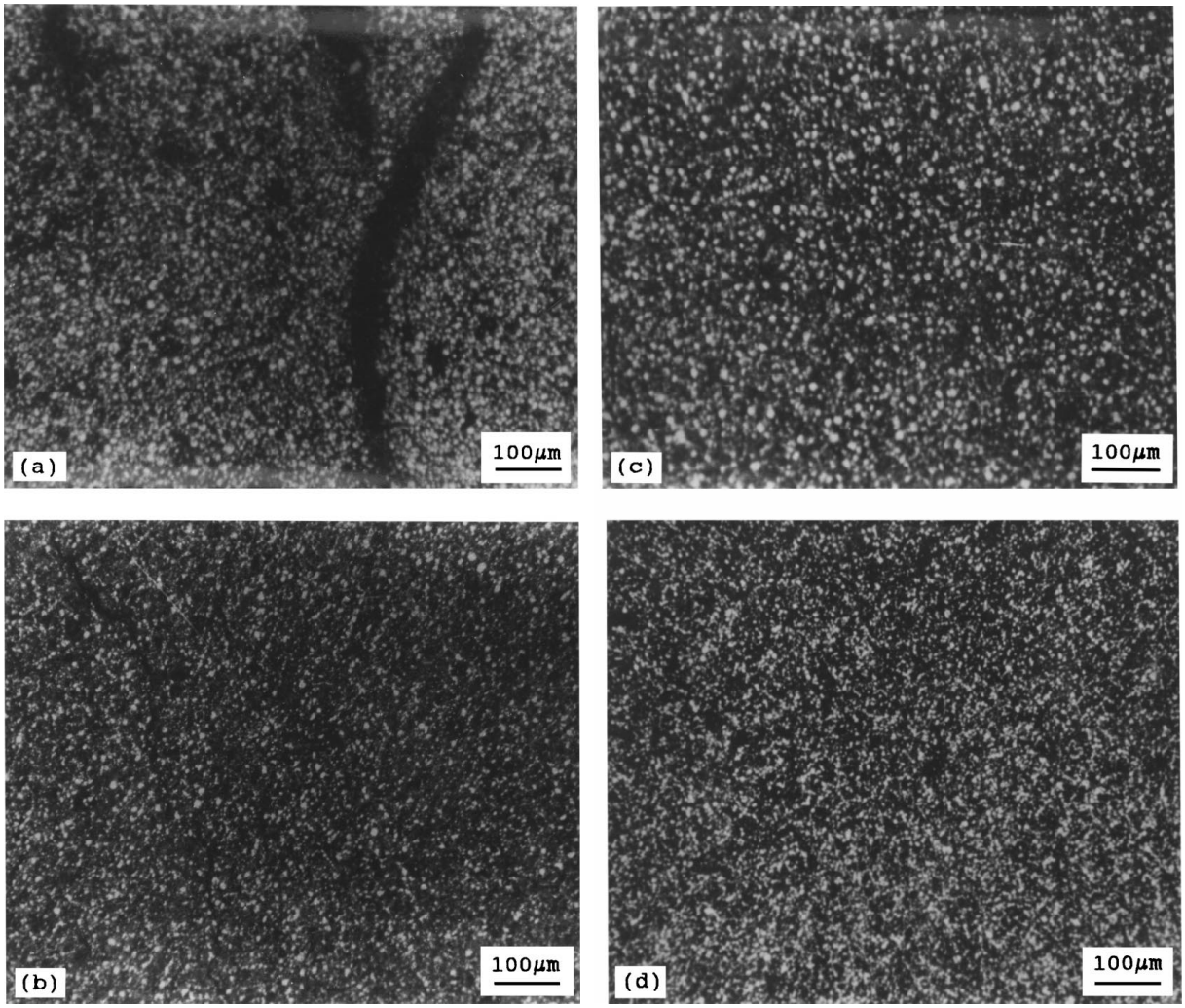

Figure 5 Optical micographs of carbonised plates (HTT=1100 °C) based on MCMB-I, (a) Uncalcined, (b) Calcined at 240 °C, (c) Calcined at 280 °C, (d) Calcined at 320 °C.

out to be almost constant (lying in the range 1.32–1.35), showing thereby that the baked density is directly proportional to the green density. Further, the values of the expected baked density are found to be quite close to the actual (observed) values.

Furthermore, it is observed that the microbeads of batches II and IIA (Fig. 6) result in carbon plates bearing some cracks, with baked densities of 1.80 and 1.78 g cm^{-3} and bending strengths of 17 and 28 MPa, respectively (Table VI). Looking at the characteristics of the microbeads of batches II and IIA (Table V) and the cracks in the resulting carbons, these high values of the baked density coupled with low values of the bending strength suggests that both these batches of microbeads (uncalcined and calcined at 215 °C) contain an excess amount of relatively low molecular weight components, like tar oil constituents and toluene solubles, which while improving the packing and fusion of the microbeads during compaction (as seen from relatively higher values of the green density) also result in the formation of cracks in these carbons because of their elimination during the carbonisation.

The increase in the calcination temperature from 215 (IIA) to 230 °C (IIB) results in an improvement in the bending strength of the plates to a value of 45 MPa. However, the microstructure of even these plates still reveals the presence of some cracks (Fig. 6). Further, the calcination of the microbeads at temperatures of 245 °C and higher results in more and more decrease in the entrapped tar oil constituents and other low molecular weight components (i.e., toluene soluble matter and β-resins) in the microbeads which helps in eliminating the formation of any cracks in the carbonised product, resulting thereby in an increase in the bending strength of the carbons upto a value of 84 MPa for batch-IIE (285 °C). However, for the microbeads of batch-IIF, calcined at 310 °C, the bending strength decreases slightly to 79 MPa from the highest value of 84 MPa (for batch-IIE), which could be attributed to a substantially reduced value (6.8%) of the β-resins content.

Regarding the results of the graphitised plates, Table VIII shows that the plates based on batches IIC to IIF (calcined at temperatures of 245–310 °C) possess a high density of 1.91–2.02 g cm^{-3}, high bending strength of 62–69 MPa, and a high degree of isotropy (Degree of anisotropy = 1.02–1.05), respectively. These high values of density, strength and isotropy are critical requirements expected of a high density - high strength - isotropic graphite. Thus, a calcination treatment of the mesocarbon microbeads at a temperature of 245–310 °C for a residence time of 10 min. under a reduced pressure (5 cm Hg) of nitrogen can also be regarded to be suitable for the use of

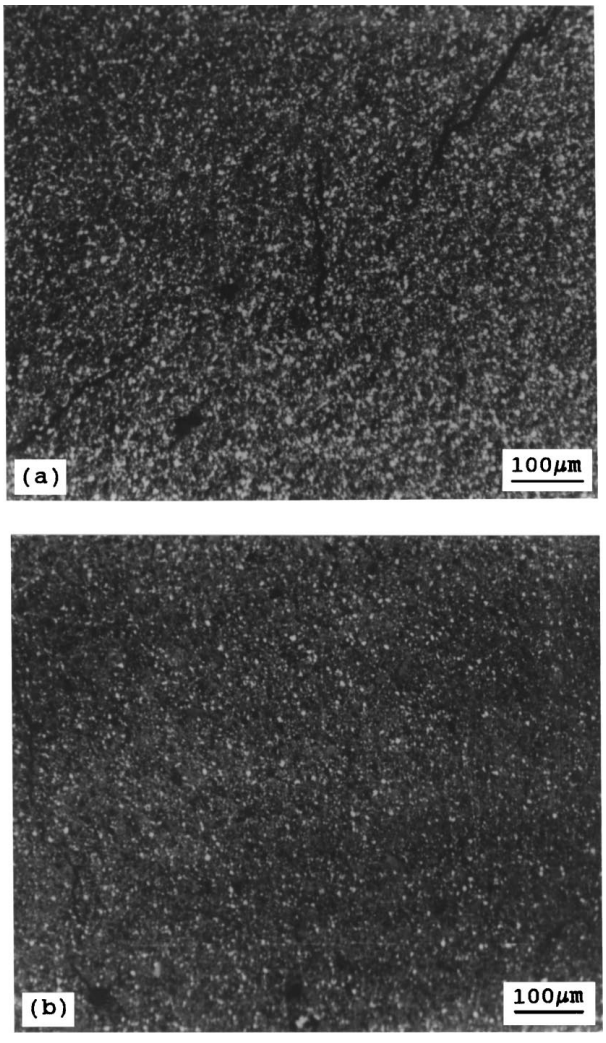

Figure 6 Optical micrographs of carbonised plates (HTT = 1100 °C) based on MCMB-II, (a) Calcined at 215 °C, (b) Calcined at 230 °C.

the microbeads in the production of high density - high strength - isotropic graphite.

4. Conclusions

1. For the given mesocarbon microbeads, obtained as insolubles with a tar oil having a boiling range of 230–270 °C, the characteristics of the final graphite depend greatly on their calcination conditions, which in turn, fix the contents of their quinoline and toluene insolubles, β-resins and volatile matter.

2. Calcination of the mesocarbon microbeads at a temperature in the range of 280–320 °C for a residence time of 30 min. under an ambient pressure of nitrogen, or at a temperature of 245–310 °C for a residence time of 10 min. under a reduced pressure (5 cm Hg) of nitrogen, removes the entrapped tar oils and adjusts the other low molecular weight components (toluene solubles and β-resins) in the microbeads, such that the calcined microbeads possess a quinoline insoluble content of 83.6–89.8%, toluene insoluble content of 94.4–99.7%, β-resins content of 6.8–11.9% and a volatile matter content of 10.2–13.5%. Such microbeads then lead to a monolithic graphite possessing a bulk density of 1.91–2.02 g cm^{-3}, bending strength of 62–70 MPa, Shore hardness of 58–69, electrical resistivity of 2.1–2.6 mΩ cm and a degree of anisotropy of 1.02–1.05.

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