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Binderless moulding of green cokes delivered from solvent refined coal and ethylene tar pitch

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Green cokes, derived from the co-carbonization of Solvent Refined Coals with ethylene tar pitch, have been moulded into discs without using a binder. Cokes with a range of size of optical texture have been prepared by control of the ratios of the two components of the carbonization blend. The appearance of the discs was assessed by optical and scanning microscopy after calcination to 1200° C. The most acceptable disc was prepared by moulding carbon of a heat treatment temperature (HTT) of 440° C. With cokes of HTT $<$ 440° C excessive dilation adversely decreased the density of the disc. With cokes of HTT $>$ 440° C, dimished cohesion of the coke grains prevented the development of a strong disc on calcination. It is considered that the presence of benzene-soluble (BS) and benzene-insoluble/quinoline-soluble (BI/QS) fractions in the pitch systems contribute to cohesion of coke particles having a HTT of 440° C.

1. Introduction

Anisotropic graphite, in its various forms, is an indispensable material for many industrial purposes [1, 2]. Recently carbonaceous materials with isotropic properties have been developed for use in nuclear reactors, electric discharges, drilling bits and chemical crucibles [3, 4]. These materials should possess a high density and strength together with moderate graphitizability [5]. Procedures used to make these materials fall into two categories; binderless moulding of suitable green cokes, and repeated impregnation after the moulding with a binder pitch.

In the present study, the moulding properties of green coke, prepared by the co-carbonization of two pitch materials, were studied to develop a new method of production of isotropic carbonaceous materials. The present study was based on the following ideas.

(a) The optical texture of green cokes influences the grain shape after grinding, as well as their graphitizability. Optical texture can be controlled by co-carbonization of suitable pitches in predetermined ratios [6, 7, 8]. Grain shape may be a major factor in determining closed and isotropic packing in moulding procedures.

(b) The adhesive properties of green cokes can be adjusted by varying their heat-treatment temperature (HTT). This is because the extent of their volatile contents and their fusibility before the calcination influence moulding properties. These can be determined by knowledge of the amounts and quality of their fractions, i.e., the hexane-soluble (HS), benzene-soluble (BS), benzene-insoluble/quinoline-soluble (BI/QS) and quinoline-insoluble (QI) fractions [9].

2. Experimental proceedures

2.1. Materials

SRC (Solvent Refined Coal from West-Kentucky coal) was extracted with benzene using a soxhlet until the filtrates became colourless, in order to obtain the benzene-insoluble fraction (BI), which was free from quinoline-insoluble (QI) material.

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TABLE I Some properties of samples

	Elemental analysis (wt %)				BS fraction (%)	AMW*
	C	H	N	(S + O)		
Ethylene tar	92.7	7.2	0.1	nil	100	230
SRC-No. 5	86.9	5.6	1.50	6.0	–	–

*Averaged molecular weight.

Ethylene tar (ETP) was supplied by Koa Oil Company. Analyses of these materials are presented in Table I.

2.2 Carbonization and calcination

SRC-BI/QS and ETP, dispersed in benzene, were mixed in a mortar. After removal of benzene under vacuum, the mixture (5 g) was transferred into a pyrex tube, of 30 mm diameter and 300 mm height, to be carbonized to green coke under nitrogen in a vertical furnace. The heating rate and soaking time were 150° C h^{-1} and 0.5 h, respectively. Moulded green coke (a disc form) was calcined at 1200° C under nitrogen in a horizontal furnace, the heating rate and soak time being 600° C h^{-1} and 0.5 h, respectively.

2.3 The moulding of green coke

The green coke (1.5 g) was ground in an automatic mill to pass a 200 mesh sieve and moulded in a press to a disc form (of 20 mm diameter and 4 mm thickness) at room temperature under 400 kg cm^{-2} pressure. Another moulding pressure (of 200 kg cm^{-2}) and grain size (passing 100 mesh sieve) were also examined.

2.4 Some properties of the disc after calcination

The bulk density of the disc was described by its weight to volume ratio, where the volume was calculated from its diameter and thickness. Apparent porosity was measured by the water penetration method. A disc was immersed in boiling water for 3 h, and then in cold water for 10 h in order to saturate it with water. The weight difference of the disc after saturation and in water (without the saturation procedure) is assumed to be the apparent porosity [9]. A cuboid (with a width of 5 mm, thickness of 3 mm and length of 5 mm), which was prepared from the disc calcined at 1200° C, was used for the measurement of the compressive strength with a Toyo Baldwin tensilon-UTM-25000. The compression speed was 0.2 mm min^{-1}. The cross-section and pressed surface of the disc before and after the calcination were observed with a scanning electron microscope (SEM) (JEOL JSM-25S).

3. Results

3.1. Optical textures of co-carbonized green cokes

Co-carbonizations of SRC-BI/QS and ETP of different mixing ratios and single carbonizations of SRC-BI/QS, and SRC-BI/QS washed with tetrahydrofuran (THF), produced green cokes with different optical textures. Micrographs of these cokes are shown in Fig. 1. Althouth the coke produced solely from SRC-BI/QS showed a fine mosaic texture (see Fig. 1b), the size of anisotropic unit could be modified. For example, as shown in Fig. 1a, the size of the optical texture decreased when SRC-BI/QS was washed with a mixture of THF (1 part) and benzene (3 parts) before carbonization. Co-carbonization of SRC-BI/QS with ETP (which yielded a coke with needle-like texture in single carbonization), enlarged the size of optical texture (see Fig. 1c). By increasing the mixing ratio to two parts SRC-BI/QS to three parts ETP from three parts SRC-BI/QS to two parts ETP the size of optical texture could be further enlarged (see Fig. 1d). Thus, any desired size of anisotropic units could be prepared from the same source by co-carbonization, or by pretreatment.

A mixture of SRC-BI/QS and ETP (3 to 2), which gave a fine mosaic texture (10 μm diameter), was carbonized to prepare the green coke used for moulding. Micrographs of the mouldings are shown in Fig. 2. The green coke prepared above 460° C, had an anisotropic optical texture over the entire surface. Some isotropic regions still remained in the coke prepared between 440 and 450° C.

Optical textures are compared before and after calcination in Fig. 2. The optical textures were found to be homogeneous fine-mosaics of similar unit-size for the different values of HTT used in the green coke preparation.

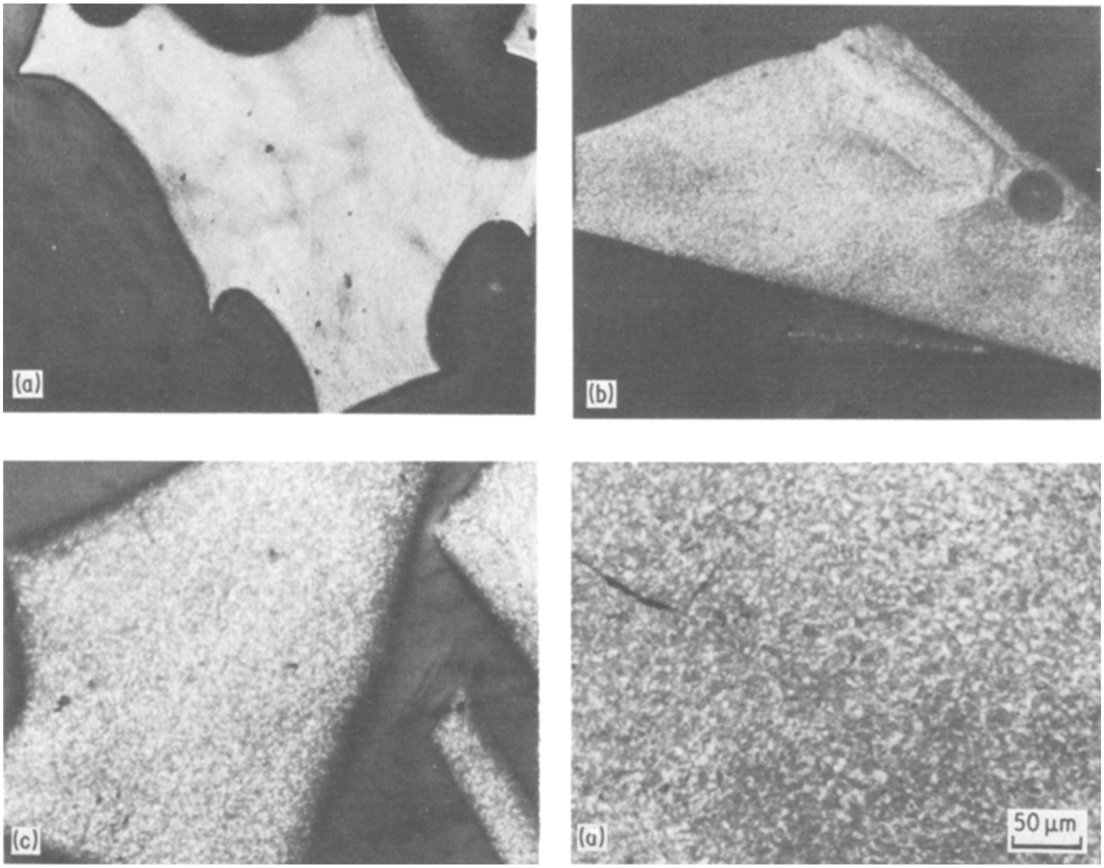

Figure 1 Optical micrographs, using crossed-Nicols, of cokes obtained from single carbonization and co-carbonization with SRC-BI/QS and ETP. (150° C h^{-1} heating rate, carbonized at 600° C for 2 h) (a) SRC-BI/QS washed with a THF–Benzene mixture (mixing ratio = 1–4), (b) SRC-BI/QS, (c) SRC-BI/QS–ETP (3–2), (d) SRC-BI/QS–ETP (2–3).

3.2. Moulding properties of green cokes

The moulding properties of green cokes prepared at different HTT values are compared in Figs 3, 4 and 5, where a photograph of the mouldings and an SEM of their surface and cross-section are given. Green cokes prepared at 420 to 460° C were moulded into a hard disc. Cokes prepared at temperatures higher than 480° C lost their adhesion. The discs from green cokes prepared at a lower HTT (420° C and 430° C), when heated up to 1200° C, became dilated and considerably deformed. Thus, a HTT of between 440 and 460° C is most suitable for the preparation of green cokes.

The cross-section of the discs observed by the SEM, clearly illustrates the different features of green coke assembly. Figs 4a, b show that whole grains are firmly attached to each other and their boundaries can hardly be detected. Individual grains however, are clearly distinguishable in the disc made from the coke prepared at 460° C, as shown in Fig. 4c. Many fissures are observable in the disc made from the green coke prepared at 460° C, although several grains form conglomerates.

The surfaces of discs after calcination at 1200° C look essentially unchanged although some voids are observable in the discs made from green cokes prepared at 440 and 450° C (figs 5a and b). In contrast, the electron micrographs made of the cross-sections clearly distinguish the discs made from green cokes prepared at 440 and 450° C, respectively. The grains fuse together tightly in the former disc after calcination, but remain unfused in the latter disc.

Grain shapes of green cokes ground in an automatic mill depend also on the HTT. Grains of the green cokes prepared at low HTT (440 and 450° C) were spherical; at high HTT (460° C and 480° C), the grains were much more angular.

BS, BI/QS and QI contents in the green cokes

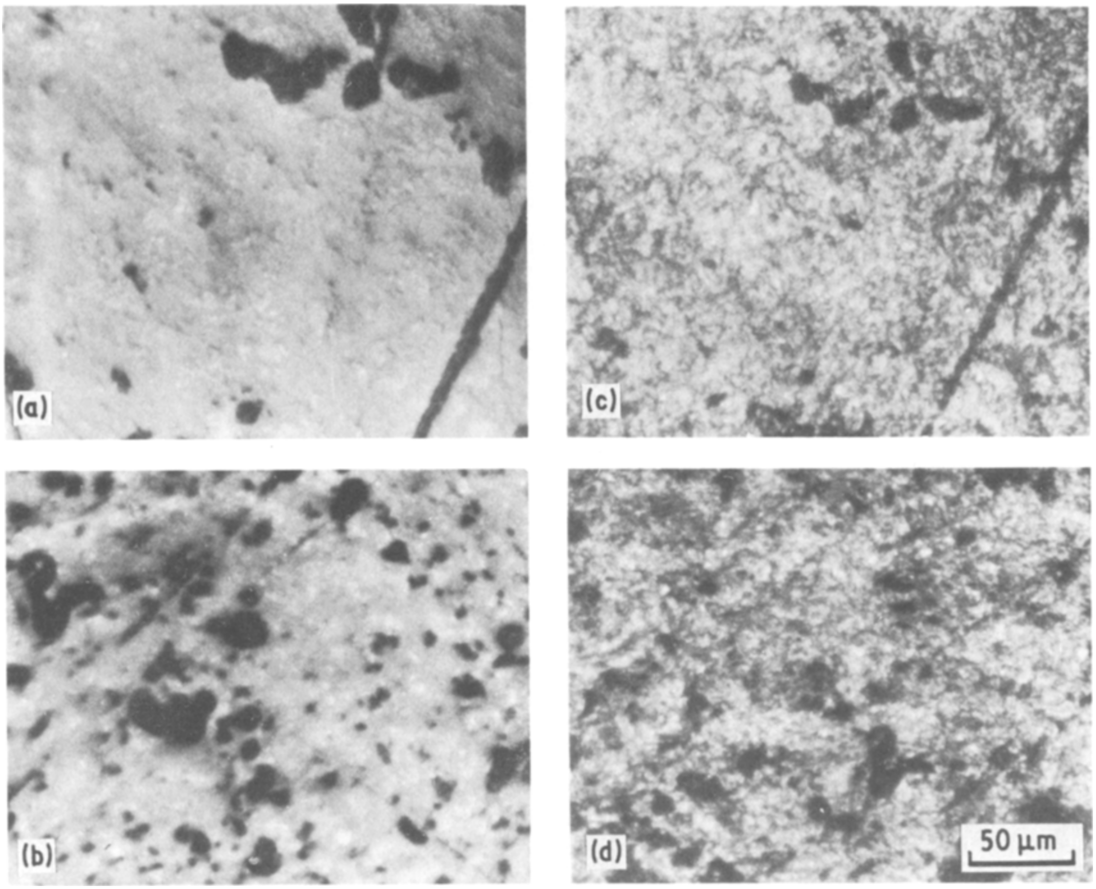

Figure 2 Optical micrographs using crossed-Nicols, of the surface of discs moulded under 400 kg cm^{-2} from SRC-BI/QS and ETP (3–2) (a) before calcining, carbonized at 440° C for 0.5 h, (b) before calcining, carbonized at 450° C for 0.5 h, (c) after calcining, carbonized at 440° C for 0.5 h, (d) after calcining, carbonized at 450° C for 0.5 h.

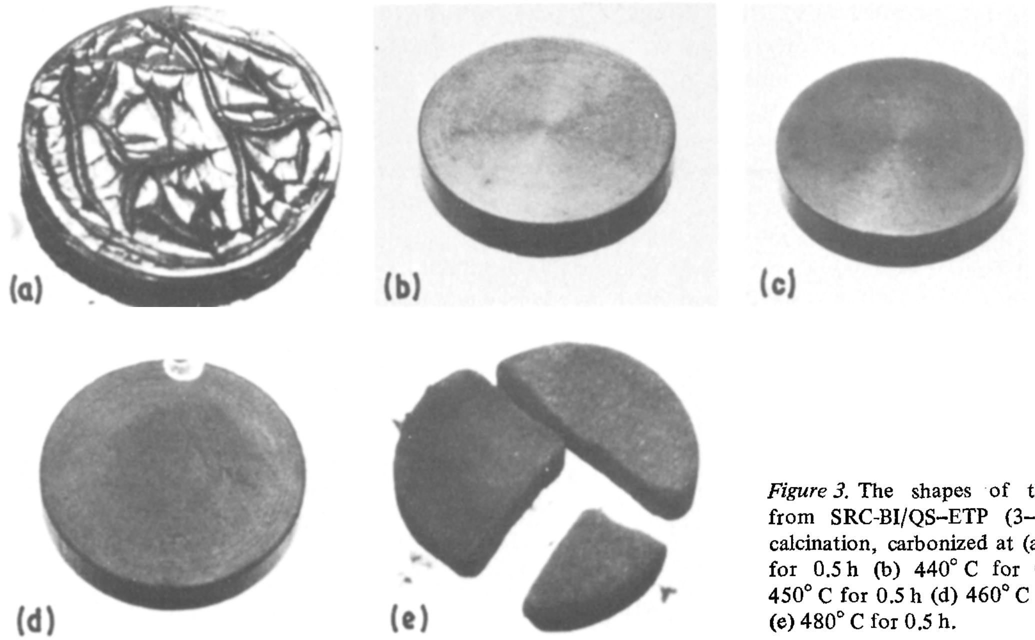

Figure 3. The shapes of the disks from SRC-BI/QS–ETP (3–2), after calcination, carbonized at (a) 430° C for 0.5 h (b) 440° C for 0.5 h (c) 450° C for 0.5 h (d) 460° C for 0.5 h (e) 480° C for 0.5 h.

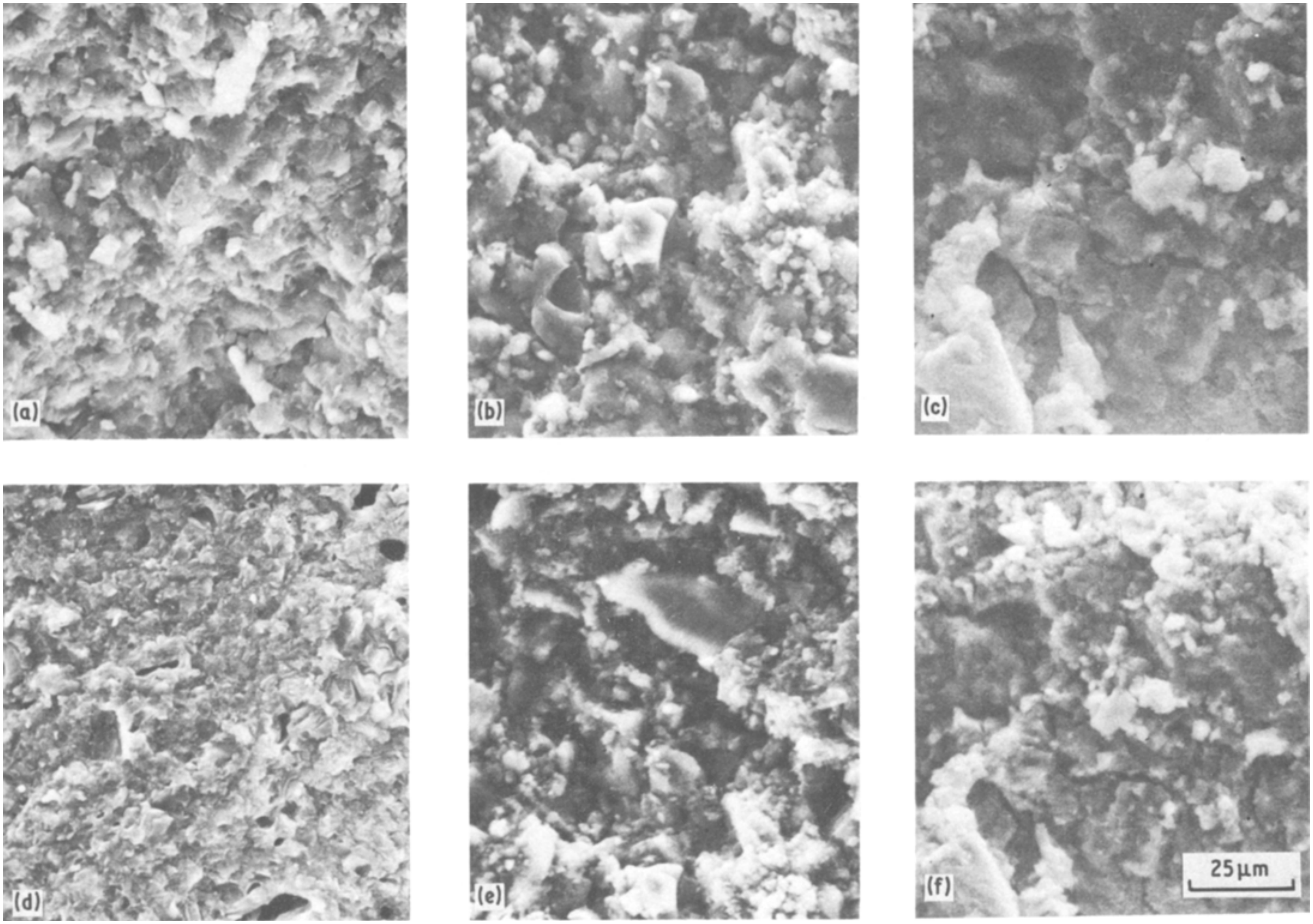

Figure 4 **SEM photographs of cross-sections of discs moulded under 400 kg cm^{-2} from SRC-BI/QS–ETP (3–2) (a) before calcining, carbonized at 440° C for 0.5 h, (b) before** calcining, carbonized at 450° C for 0.5 h, (c) before calcining, carbonized at 460° C for 0.5 h, (d) after calcining, carbonized at 440° C for 0.5 h, (e) after calcining, carbonized at 450° C for 0.5 h, (f) after calcining, carbonized at 460° C for 0.5 h.

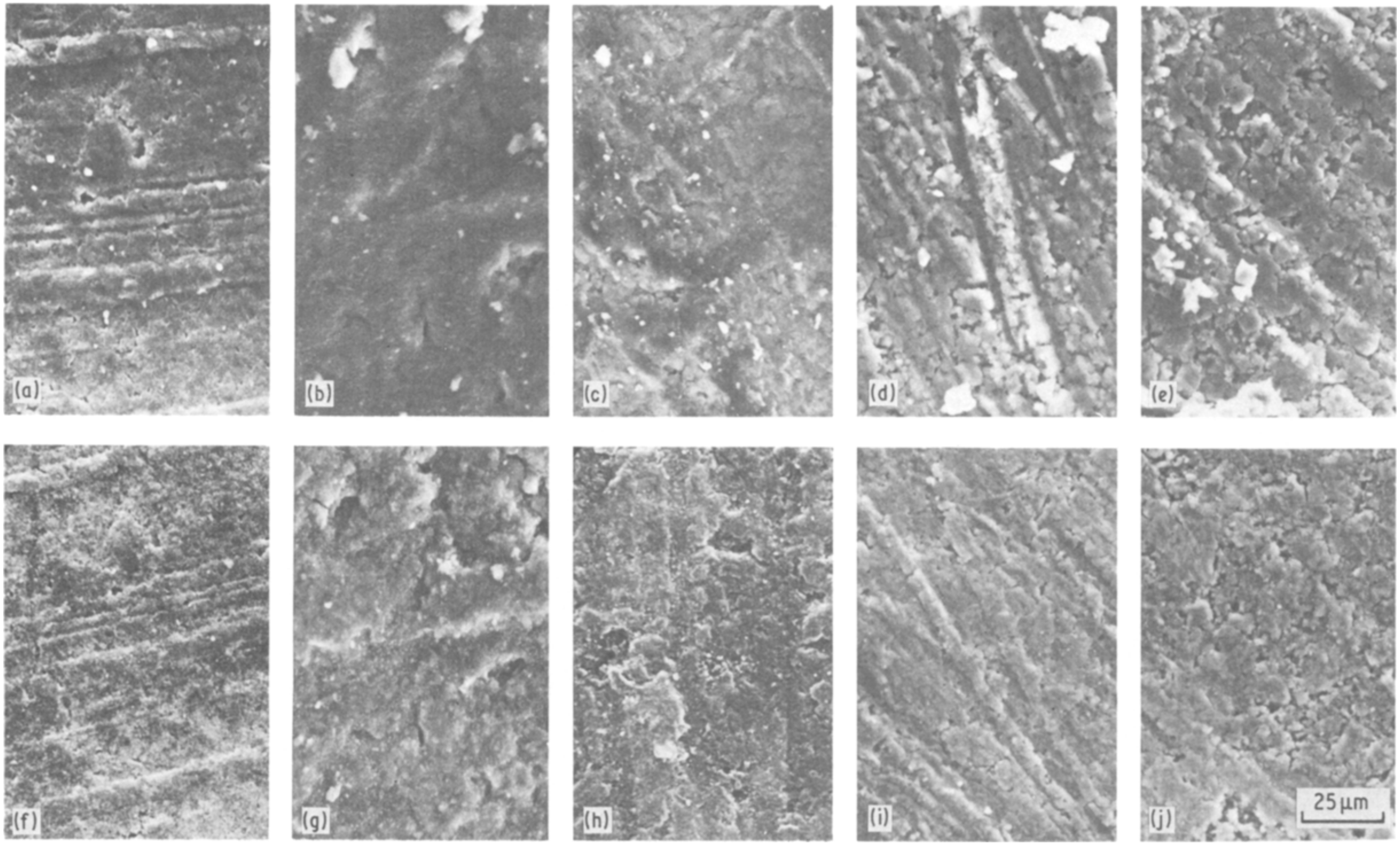

Figure 5 SEM photographs of surfaces of the discs prepared from SRC-BI/QS–ETP (3–2), carbonized at 440° C for 0.5 h fractionated with some solvents (a) before calcination, original, (b) before calcination, HI, (c) before calcination, BI, (d) before calcination, BS/QI, (e) before calcination QI, (f) after calcination, original, (g) after calcination HI, (h) after calcination BI, (i) after calcination BS/QI, (j) after calcination, QI.

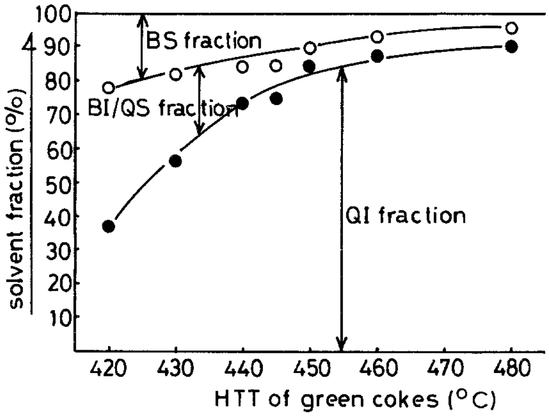

Figure 6 Relationship between carbonization temperature and solvent fractionation yield of green cokes prepared at variable temperatures.

prepared at various temperature are illustrared in Fig. 6. Amounts of BS and BI/QS fractions in the green coke decrease gradually as the HTT for the preparation of green coke increases and in turn the QI contents sharply increases over a HTT of 420° C.

Moulding properties of green cokes (prepared at 440° C) free from HS, BS/QS and QS, respectively, are compared with those described above. Micrographs of the surfaces of the discs prepared from such green cokes are shown in Fig. 5. Green cokes free from HS (Fig. 5b) have essentially the same appearance as the original coke with somewhat fewer voids, indicating the minor role of this fraction in adhesion. This fraction may volatilize during the calcination, probably leaving voids. Elimination of the BS fraction creates crevices, suggesting some contribution by this fraction to the adhesion. The surface of the discs from coke from QI (Fig. 5e) was rough, the coke grains being clearly distinguished. An important role of the BI/QS fraction for adhesion during calcination is therefore suggested.

3.3. Some properties of discs

Weight-losses and shrinkages of diameter and thickness of the disc caused by calcination are shown in Fig. 7. Both values decreased monotonically with increasing HTT of the green coke.

Although bulk densities of the discs before calcination were about 1.1 to 2 g cm^{-3} regardless of the HTT of the green cokes, these values, after calcination, tended to decrease with increasing HTT of the green cokes above 440° C.

Compressive strengths of the discs after calcination are illustrated in Fig. 8, where a sharp dependence on HTT is indicated. The green coke prepared at 440° C gave the highest strength, about 10 t cm^{-2}.

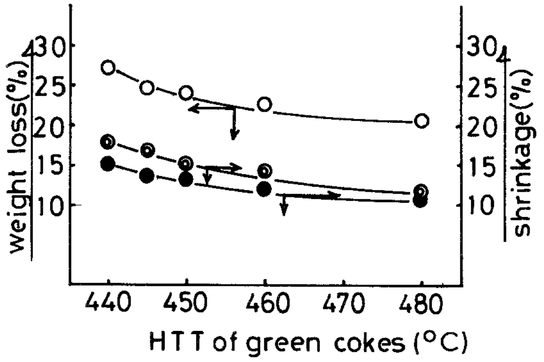

Figure 7 Relationship between weight loss and shrinkage ratio of the discs by calcination at 1200° C o: weight-loss, o: diameter shrinkage, •: thickness shrinkage.

4. Discussion

4.1 Co-carbonization to produce green cokes of adjusted optical texture

Marsh [6] and Mochida *et al.* [10] commented upon the importance of co-carbonization for production of needle and blast furnace cokes of better quality in terms of the development of anisotropic

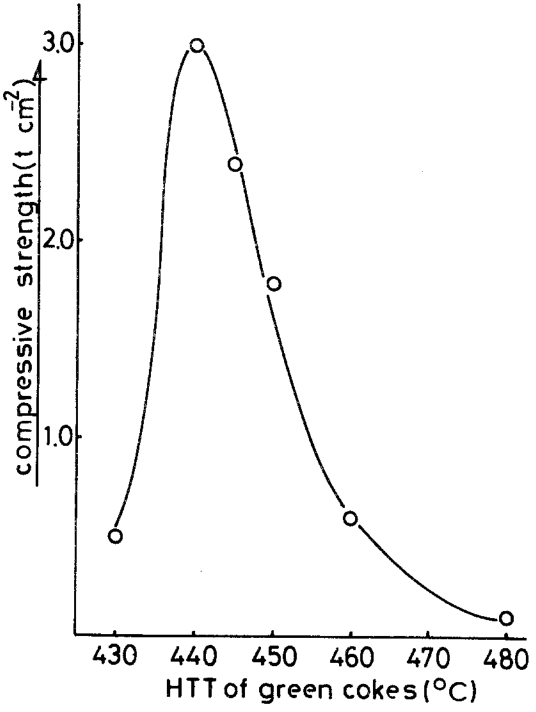

Figure 8 Compressive strength of the moulded discs calcined at 1200° C.

optical texture. This study uses co-carbonization techniques to modify the anisotropy with rather small effect, for the isotropic properties of mouldings. The optical anisotropy of the green coke developed, or to be developed in the later heat treatment, was essentially determined by the mixing ratio of ETP and SRC/QS, but was independent of final HTT. The ETP dissolves the SRC/QS during the carbonization to give the homogeneous feature of the green coke. However their poor compatibility limits the size of anistropic unit.

Since the flow texture of green coke tends to produce elongated grains when it is ground as reported previously [11], mechanical anisotropy due to the oriented arrangement of the grains, each of which has a preferred orientation of lamella, may originate when they are moulded, unless the green coke is finely ground. In contrast, the fine mosaic texture of the green coke tends to produce spherical grains of similar size to the anisotropic unit when ground, and some isotropy remains. If the green coke is made up entirely of fine mosaic the grains tend to be somewhat angular. Thus, the optical texture of the green coke can influence the isotropic properties of the moulds. Honda *et al.* [12], proposed that small anisotropic spheres produced after quinoline extraction were suitable materials for mechanically making isotropic carbon mouldings. The fine grain mosaic can behave similarly, with the advantage of a simple procedure and high yield.

4.2. Adhesion of grains in the binderless moulding

There may be several properties required by green coke for production of carbon of high density and strength for binderless moulding. They are,

(a) High density of packing in the mould,

(b) deformable properties under the pressure,

(c) controlled fusibility in the early stages of calcination to allow adhesion of grains without dilation and deformation of the bulk form, and

(d) isotropic shrinkage in the later stage of the calcination.

The first factor may require spherical shapes which are of fine grain mosaic optical texture, surrounded by isotropic material. The second and third factors may require a suitable selection of parent materials and HTT. The solvent-fractionation can be a guide-line for the preparation of such a green coke. Although the hexane-soluble fraction may help the fusion of green coke, it provides sometimes too much fluidity and very probably pores or voids by volatilization below 600° C. The benzene soluble fraction may behave similarly, however, its volatile content may be less. The heaviest portion of BS, of a controlled amount in green coke, can be one of the most important components in retaining the most desirable fusion state of the green coke, in co-operation with BI/QS. The quinoline insoluble material can not be fusible by itself, but is still deformable when the BS and BS/QS fractions are present. When it is produced at relatively lower temperatures, its high coke yield can give it the role of frame work for moulding. Thus, extraction of undesirable fractions can be helpful in the preparation of suitable green cokes.

Shrinkage of the carbon during the calcination can not be discussed adequately at this stage. This phenomenon is quite important in the production of mouldings of high density, otherwise micropores are produced. The shrinkage may be assumed to be connected with graphitization. Graphitizability can be also controlled by the selection of starting materials, their combination and HTT conditions.

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