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Influence of grinding on the graduation graphitization and densification of coke powder

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Petroleum coke powder, made by the delayed coking method at about 500° C, was ground for various times from 15 min to 44 h. Carbon solids were made from the ground coked powder compacts and heat-treated at 1000 to 2800° C without the use of binder materials. The coke particles ground for a considerable time had a spherical appearance and an amorphous structure, and showed non-graphitizability. These ground powders were easily densified and hard carbon solid could be obtained by heat-treatment. However, if the coke powder was pre-heat treated above about 600° C before grinding, no densification occurred and the powder graphitized as well as non-ground ones. The hard carbon solids made from powder ground for 44 h had a bulk density of 1.71 $\mathrm{g\,cm^{-3}}$, Shore hardness of 120 and bending strength of about 700 $\mathrm{kg\,cm^{-2}}$ at a heat-treatment temperature of 1000° C. These values changed with increasing heat-treatment temperature to a bulk density of 1.93 $\mathrm{g\,cm^{-3}}$, Shore hardness of 90 and bending strength of 500 $\mathrm{kg\,cm^{-2}}$ at a heat-treatment temperature of 2800° C.

1. Introduction

Sinterability of raw powder is known to be improved by grinding treatment for some ceramic materials. Although the influence of grinding the carbon powders on the subsequent graphitization behaviour has been reported by some workers [1–3], there is little knowledge on the sintering and densification behaviour of ground carbon powders which are expected to be more sinterable.

Conventional carbon and graphite materials are normally made using a calcined filler coke and binder, such as coal tar or petroleum pitch, through carbonization and graphitization processes. In these complex commercial processes, the carbon products contain large voids which weaken the strength and the ability to withstand stress. Therefore, in order to make a high-density carbon, various techniques have been used in the fabrication, such as repeated impregnation with pitch and heat-treatment in an autoclave, use of high-yield pitch, or the filling-up of pores with a deposition of pyrolytic carbon. If a new sintering method can also be established for alloy and ceramic powders, the processing period could be shortened and dense, strong carbon materials could easily be manufactured with no need to use a pitch binder phase in the process.

This paper reports the influence of grinding on some characteristics both of carbon powders before the calcining stage and of carbon solids made from those ground powders without using binder phase in the sintering process.

2. Experimental procedure

The starting material used in this study was petroleum needle-coke (green-coke) powder (of 60 to 100 mesh size), manufactured by a delayed coking method at a temperature of about 500° C and then calcined, which contains approximately 10% volatile matter. The apparent density of the grains is 1.35 $\mathrm{g\,cm^{-3}}$.

Samples of the coke powder of weight 5 g were ground in an air atmosphere for times between 15 min and 44 h using an automatic tungsten carbide mortar with an inner diameter of 140 mm and a depth of 65 mm. After grinding the powder was

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compressed into either cylindrical pellets of diameter 20 mm and height about 13 mm or rectangular pellets of diameter 30 mm, height 30 mm and thickness 10 mm, under a pressure of 2000 kg cm^{-2} using a die and plunger. The compact was surrounded by calcined coke powder in a graphite crucible and was heat-treated at 1000° C in an Ar-gas atmosphere under normal pressure. The carbon solids so formed were heat-treated again in the range of 1300 to 2800° C in a graphite furnace. The heating rate was 300° C h^{-1} up to 1000° C and 400° C h^{-1} from 1000° C to 2800° C. All the samples were held at the final temperature for 1 h.

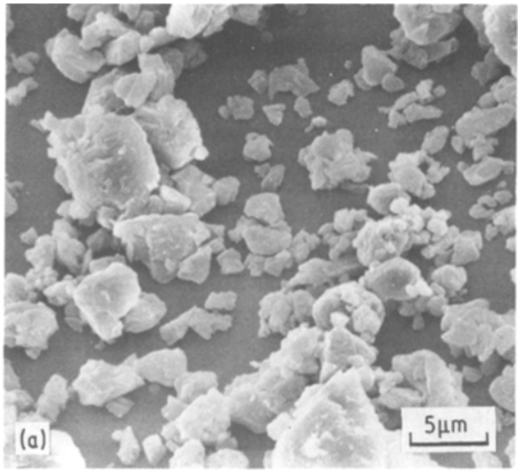
The pre-heat-treatment temperature of the raw powder before grinding was also investigated on graphitization and densification. The powder was pre-heat-treated from 450 to 900° C with a heating rate of 3° C min^{-1} in an Ar-gas atmosphere. These powders with different pre-heat-treatment temperatures were examined using the same procedure as mentioned above.

X-ray diffraction profiles were measured using an X-ray powder diffractometer with monochromatic CuKα radiation. A mercury porosimeter was used for the measurement of the pore-size distribution. Porosity was calculated from measurement of the bulk volume and the water content of the sample after boiling in water for 3 h. Compressive strength was measured with a cross-head speed of 0.5 mm min^{-1}. Bending strength was measured by a three-point bend test with a span distance 20 mm on the rectangular specimens of width 8 mm and thickness 5 mm. Electrical resistivity was measured by the constant current potentiometric method using specimens of dimensions 25 mm x 10 mm x 5 mm.

3. Results

3.1. Influence of grinding on the coke powder and the green compacts

Fig. 1 shows changes of the shape and size of the raw coke particles, fabricated at about 500° C, with grindimg time. The original coke particles of size 50 to 250 μm were ground for 15 min to produce particles of size 1 to 10 μm; however, in 15 min the size distribution was relatively broad and most of the particles still had some irregular configuration (see Fig. 1 a). After grinding for 5 to 6 h the particles had a relatively uniform size of 1 to 5 μm (see Fig. 1b). When the grinding time was prolonged for more than 5 to 6 h no further size reduction was observed but the particle shapes gradually changed, becoming more nearly spherical with increasing grinding time (see Fig. 1c).



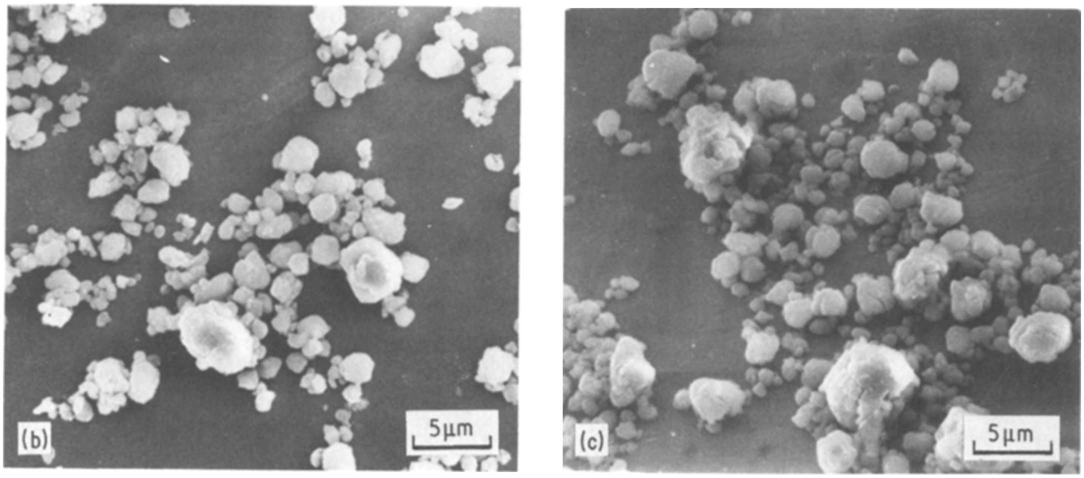


Figure 1 Scanning electron micrographs of green petroleum coke powders. (a) Ground for 15 min; (b) ground for 6 h; (c) ground for 44 h.

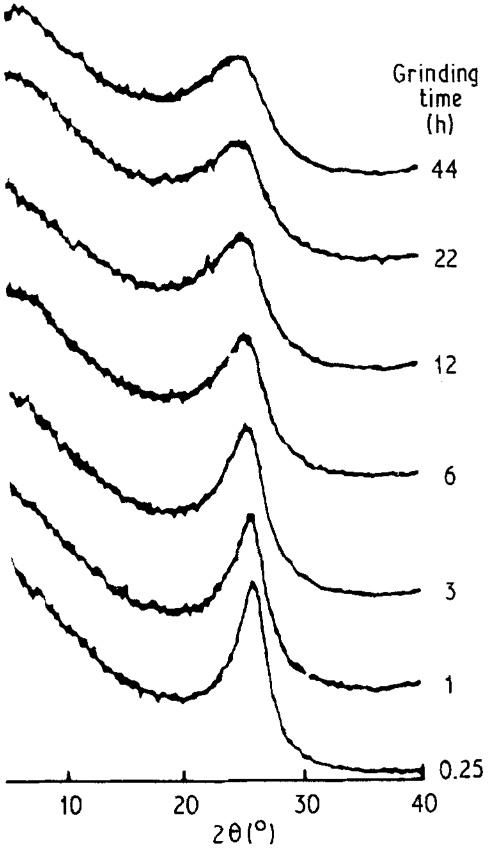


Figure 2 (002) X-ray diffraction profiles of the coke powders ground for various times.

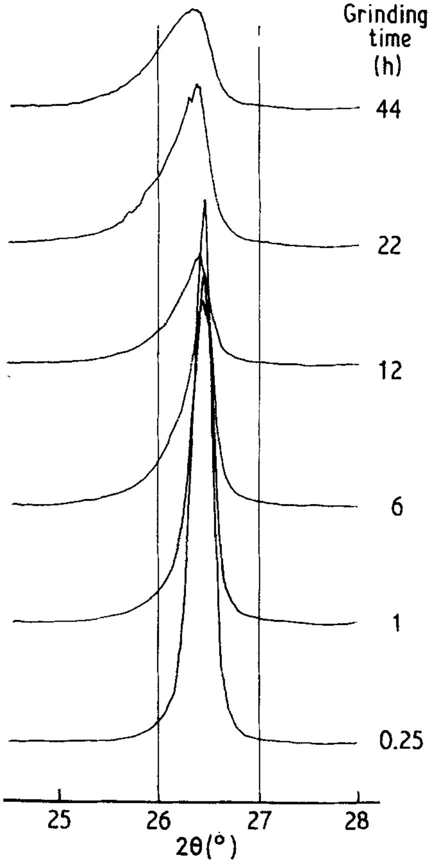


Figure 3 (002) X-ray diffraction profiles of the coke powders heat-treated at 2800° C after grinding for various times.

The (002) X-ray diffraction profile of the ground coke powder became gradually broader and shifted to lower angles with increased grinding time, as shown in Fig. 2. This suggests that the structure of coke was gradually distorted and transformed to an amorphous one by the grinding treatment.

As the coke powder is known to be graphitizing-type carbon, the ground powder once transformed to the amorphous state could not be graphitized even by heat-treatment at high temperature. Fig. 3 shows the change of the (002) peak with grinding time after heat-treatment at 2800° C of the raw powder.

It is also found that the amount of volatile matter in the original coke gradually increased with grinding time from 10% after being ground for 15 min to 17 to 18% after being ground for 44 h. The formation of a carbonyl group was detected, by infra-red (i.r.) spectral analysis of the ground powders, as shown in Fig. 4.

The green density of the ground powder compacts formed at a pressure of 2000 kg cm^{-2} increased with grinding time from 1.12 g cm^{-3} in the original state to 1.27 g cm^{-3} in 44 h. Fig. 5 shows the pore-size distributions of the powder compacts ground for 15 min and 44 h. The coke compact ground for 44 h has a relatively small average pore size, of 600 Å, and a narrow distribution range compared with the coke compact ground for 15 min which shows a wide range of pore size from 500 to about 1500 Å.

These measurements on the coke powder were made at a temperature of about 500° C. The pre-heat-treatment temperature of the raw coke powder was also found to be an important factor influencing the graphitization and compacting behaviour of the ground powder. Fig. 6 shows changes of the half-width of the (002) X-ray diffraction profile with varying pre-heat-treatment temperature for coke powders before and after grinding for 44 h. The powder without grinding shows a gentle increase in half-width, a maximum value at about 700° C and then decreases with increasing pre-heat-treatment temperature. Below

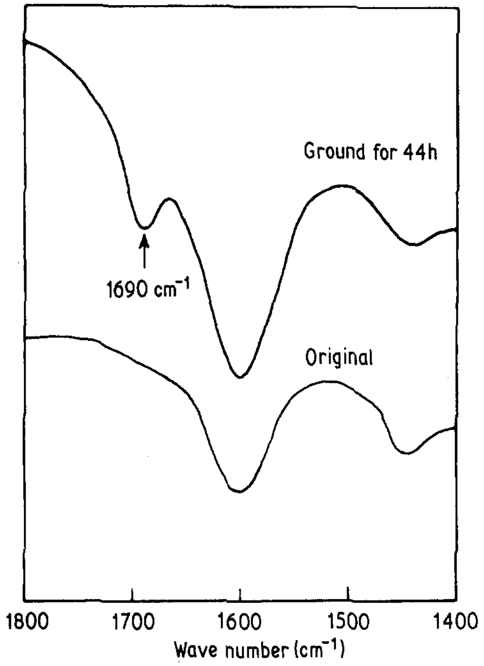


Figure 4 Infra-red spectra of the unground (original) green petroleum coke powder and green petroleum coke powder ground for 44 h.

about 550° C there is a difference between the unground and ground samples. That is, in the range below about 550° C the peak width increased remarkably for the ground powder, but no significant change was caused by grinding, above about 550° C. For the ground coke powder pre-heat-treated above about 550° C no spherical appearance of the particles was seen even after prolonged grinding, and a compact body was difficult to make. The powders pre-heat-treated above 550° C were still well graphitized even at the high temperature of 2800° C and even after prolonged grinding. Fig. 7 shows the variation of the (002) diffraction peak shape of coke powders, ground for 44 h and heat-treated at 2800° C, with pre-heat-treatment temperature. The peak shape of the ground powder pre-heat-treated at 900° C was almost the same as that of the non-ground powder.

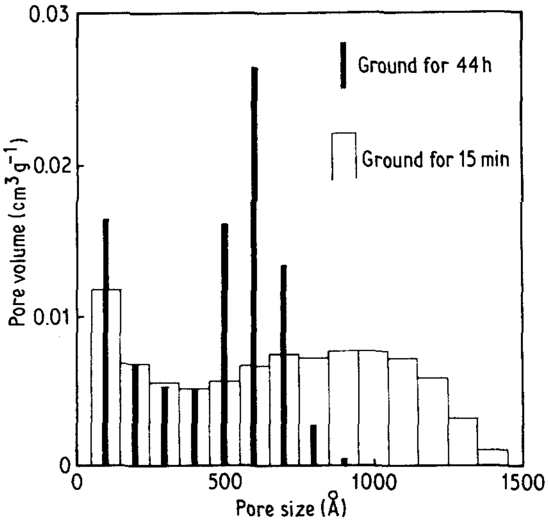


Figure 5 Pore-size distributions of the green compacts formed with coke powders ground for 15 min and 44 h.

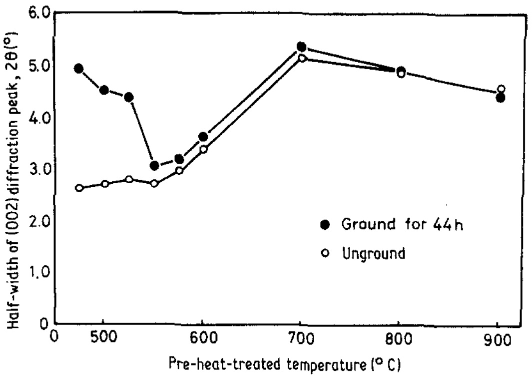


Figure 6 Changes of half-width of the (002) X-ray diffraction profiles with pre-heat-treatment temperature for coke powders before and after grinding.

These results show that grinding was only effective in enhancing the coke properties at the early carbonacious stage, at temperatures lower than about 550° C.

3.2. Heat-treated solids

The linear shrinkage of the compacts during heat-treatment up to 1000° C increased with grinding time of the raw powder from 10% shrinkage for powders ground for 15 min to 14% shrinkage for powders ground for 44 h. Cracks or shape deformation of the carbon solids were not produced in all the samples by heat-treatment.

Fig. 8 shows the changes of bulk density and porosity of the carbon solids heat-treated at 1000° C with grinding time of the raw powder. Bulk density increased, and porosity decreased, with grinding time. The compressive strength and Shore hardness also increased with grinding time as shown in Fig. 9. The coke carbon solid from the powder ground for 44 h and heat-treated at 1000° C was found to have a compressive strength of about 2700 kg cm^{-2} and a Shore hardness of about 120. These results show that the sinterability of green coke powder was remarkably accelerated by prolonged grinding.

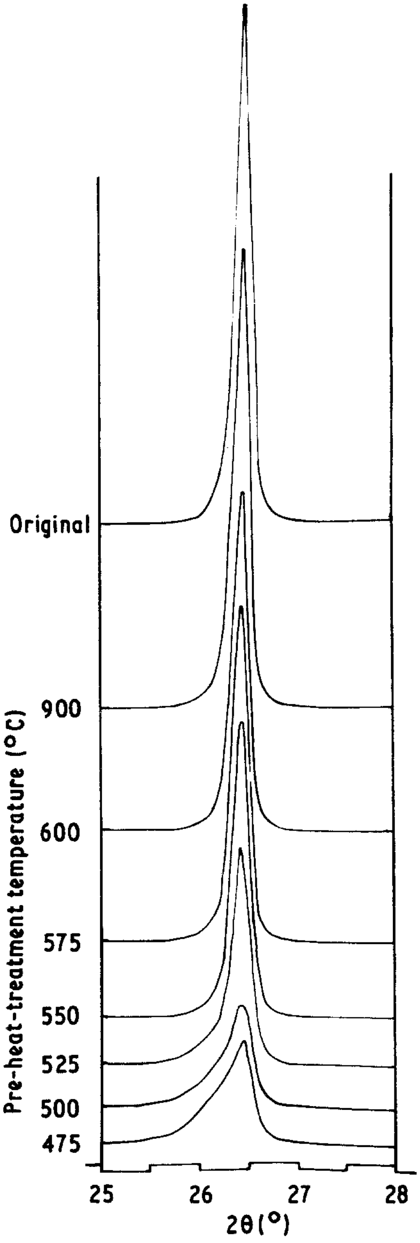


Figure 7 (002) X-ray diffraction profiles of the ground coke powders, for 44 h and heat-treated at 2800° C, after pre-heat-treatment at various temperatures.

Fig. 10 shows change of bulk density and Shore hardness of the coke carbon solid ground for 44 h with heat-treatment temperature from 1000° C to 2800° C. It shows that there is a gradual increase of bulk density and decrease of hardness with heat-treatment temperature. The bending strength remained approximately constant, at a value of 700 to 750 kg cm^{-2}, from 1000 to 1800° C and then decreased slightly to about 500 kg cm^{-2} at 2800° C, as shown in Fig. 11.

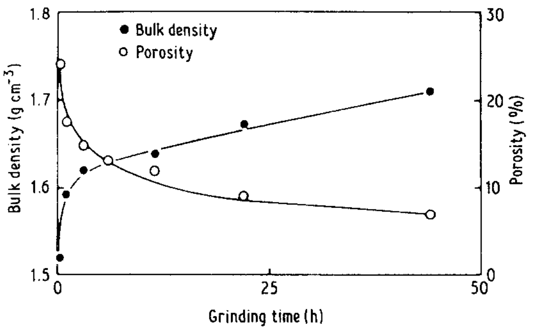


Figure 8 Changes of bulk density and porosity of the carbon solids, heat-treated at 1000° C, with grinding time of the raw powders.

Fig. 12 shows the change of electrical resistivity at room temperature with heat-treatment temperature for coke carbon solid ground for 44 h compared with those of glassy carbon made from phenolic resin [4] and conventional artificial graphite [5]. For the ground coke carbon, the resistivity has an almost constant value in the temperature range 1400 to 2200° C and then decreases slightly above 2500° C. This behaviour is similar to that of glassy carbon and artificial graphite, although, in the case of the artificial graphite the resistivity decrease above 2000° C is comparatively large.

Fig. 13 shows an electron scanning micrograph of the coke carbon solid ground for 44 h and heat-treated at 2800° C. It shows a dense texture with spherical grains in which lamella are orientated concentrically. Some small discrete pores of size less than 5 μm size are seen to exist in the grain boundary region.

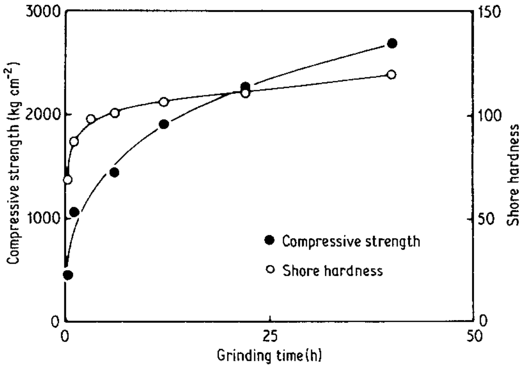


Figure 9 Changes of compressive strength and Shore hardness of the coke carbon solids, ground for 44 h and heat-treated at 1000° C, with grinding time of the raw coke powder.

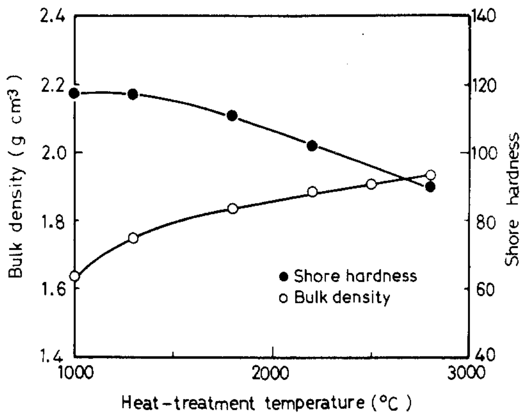


Figure 10 Changes of bulk density and Shore hardness of the coke carbon solid ground for 44 h with heat-treatment temperature from 1000 to 2800° C.

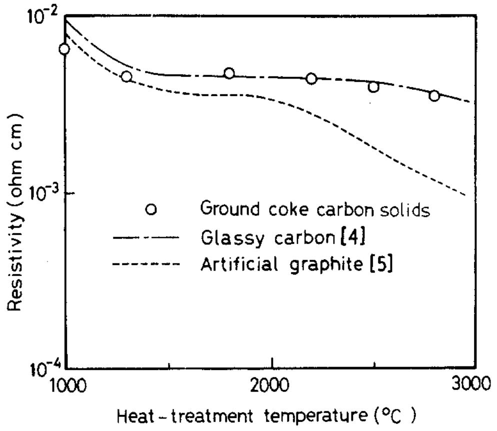


Figure 12 Change of electrical resistivity at room temperature of the coke carbon solid ground for 44 h with heat-treatment temperature.

4. Discussion

It was found that raw petroleum coke powder, which is well known as a graphitizing type carbon, was changed into a non-graphitizing-type carbon and gradually became sinterable if it was subjected to prolonged grinding.

Kmetko [6] has already observed, from an electron microscope study, that milling coke while it is still raw, that is, heat-treated to only about 600° C or lower, distorted the lamellar structure as well as the microcrystalline orientation. Our results also showed similar behaviour, indicated by broadening of the X-ray diffraction profile, and, in addition, we observed a change to a spherical shape of the particles with a relatively uniform size of 1 to 5 μm. The change to non-graphitizing-type carbon could not be made to take place for the powder pre-heat-treated above 600° C. The coke pre-heat-treated above 600° C is considered to have already acquired a relatively stable structure thus making it difficult for changes to be produced by the grinding stress. These carbon powders are easily graphitized, but not densified without the use of a binder. On the other hand, the coke powders pre-heat-treated below about 600° C are easily destroyed and transformed into an amorphous powder by grinding, but are hard to rearrange to make an ordered graphitic structure by subsequent heat-treatment at high temperature, i.e. they can be densified.

Morphological change to spherical particles with relatively uniform size seems to be an impotrant factor for densification, as the powder pre-heat-treated above 600° C did not show such spherical shape even after prolonged grinding and could not be densified. The spherical partilces are

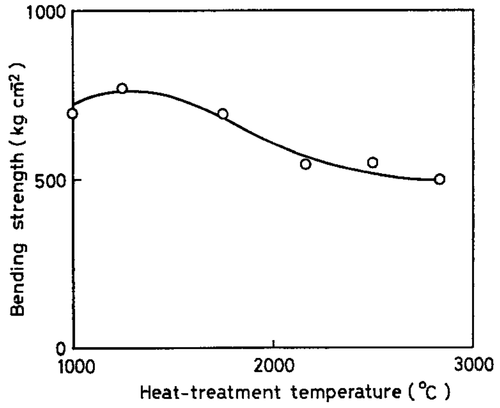


Figure 11 Change of bending strength of the coke carbon solid ground for 44 h with heat-treatment temperature.

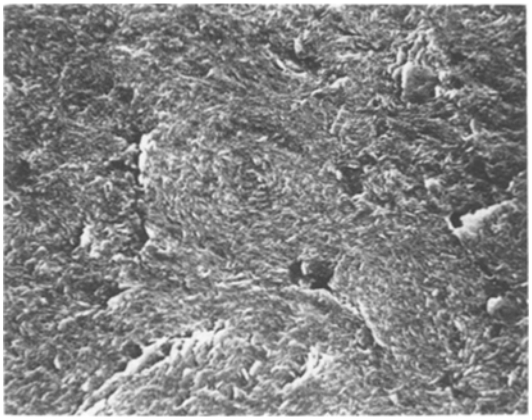


Figure 13 Electron scanning micrographs of the coke carbon solid ground for 44 h and heat-treated at 2800° C.

considered to pack closer and the green compact had a small pore size and narrow pore size distribution, as shown in Fig. 5. This close-packed green compact seems to promote sintering and results in heat-treated solids with high mechanical strengths.

Mrozowski [7] has reported that hard and dense carbon compacts can be made, without the use of a pitch binder using carbon particles, when they have surfaces containing chemically combined oxygen. In our results adsorption of oxygen on the particles was also identified, but it is not clear how much it contributed to the ease of sintering. Several per cent of volatile matter introduced by grinding might also contribute, as a liquid phase, to the sintering. In order to clarify the sintering mechanism more detailed experiments must be conducted, however, it has been shown that hard, dense carbon materials can be made by grinding raw coke powder, without the use of a binder phase.

Comparing this processing method with conventional ones, the following characteristics are observed.

(a) This process is simple and no binder phase is required;

(b) No harmful pollution problems result from the use of the process on a commercial scale since no pitch or pitch-based materials are used;

(c) It is a quick process;

(d) The carbon body made by this method is of the hard type and has properties similar to those of glassy carbon.

Carbon compacts produced using this process might be used for machine parts in place of parts manufactured from conventional hard-carbons such as glassy carbons resulting in a reduction of the production costs.

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