JOURNAL OF MATERIALS SCIENCE 27 (1992) 1161 1165

Densification of raw coke powder compacts

ICHITARO OGAWA, KAZUO KOBAYASHI
Government Industrial Research Institute of Kyushu, Shuku-machi, Tosu-shi, Saga 841, Japan

The effects of grinding on densification of a petroleum raw coke were examined. The compact of the powder ground for a short time showed large puffing during calcination below 400 °C, and no densification by subsequent heat treatment. It was found that the puffing could be suppressed by long grinding of the powder. In the compact of the powder subjected to prolonged grinding, the pore volume decreased in two temperature ranges of calcination, at 400–500 and 600–700 °C. The first decrease seems to be attributed to softening and volume reduction due to carbonization of quinoline-soluble components among the coke grains. The second decrease suggests that the sintering due to solid state material transport, such as viscous flow and plastic deformation, takes place in addition to gas-phase material transport. The increase in bulk density at temperatures over 1000 °C was mainly due to contraction of constituent grains in which micropores decreased, not a decrease in pore volume of the compact. The most remarkable effect of grinding on densification of the raw coke was the suppression of puffing during the calcination process.

1. Introduction

Carbon materials are normally made from calcined filler coke and petroleum pitch binder through calcination and graphitization processes. The carbon products from these commercial processes contain large voids which weaken the mechanical strength. Therefore, various special techniques have been used in the fabrication, and enabled us to obtain carbons of high density and strength. However, these fabrication processes are complicated, and, therefore, the products are of high cost.

Some problems arise in making dense carbons because carbon powders are normally hard to sinter without a binder. We reported previously that the raw coke became sinterable and could be transformed into dense carbons without a binder phase if it was subjected to prolonged grinding [1, 2]. An application of this grinding technique enabled us to industrialize new carbon/ceramic composites with high density and high oxidation resistance [3].

The grinding of raw coke powder definitely affects the densification and characteristics of the carbon and composites materials. In the present work we studied the effect of grinding on the densification of the compacts of petroleum coke powder.

2. Experimental procedure

The raw coke used in the present experiment was petroleum raw coke of needle type (green coke) manufactured by a delayed coking process at 460 °C, which contains 12% volatile matter. The raw coke was ground for 15 min and 44 h using a tungsten carbide mortar. The ground powder was treated with quinoline at 70 °C for 20 min in order to extract soluble components, and then the filtrate was removed by centrifugal separation. After repeating this treatment four times, the residue was washed with warm benzene and acetone, and dried at 200 °C in a vacuum.

The powders were compacted under a pressure of 200 MPa by use of a die and plungers, and then subjected to calcination at 1000 °C and subsequent graphitization up to 2800 °C in argon. The heating rate and holding time were 3 °C min^{-1} and 1 h, respectively.

On a green compact 10 mm long and 6 mm × 6 mm cross-section, dimensional changes occurring during calcination were measured by use of a dilatometer with a quartz push rod and a supporting tube in an argon gas atmosphere. The test compacts were heated by cyclic heating, from 50 °C to the holding temperatures which were stepped up to 950 °C in increments of 50 °C. The holding time at each temperature was 30 min, and the heating and cooling rates were both 20 °C min^{-1}. The dimensional changes with cyclic heating were corrected for instrumental error by comparison with a standard.

The percentage of total amount of pores in the compacts, open and closed pores, was calculated using

$$P = 100(1 - D_s/D_p) \qquad (1)$$

where D_s is the bulk density of the compact, and D_p the density of the grains which were heat treated without compacting at the same temperature as the compact. D_p was measured using a pycnometer with *n*-butyl alcohol.

The average diameter of aromatic carbon layers in the coke was estimated by Diamond's method of X-ray diffraction [4]. The rate of methane formation during calcination was measured using gas chromatography. A 0.5 g sample was heated at 5 °C min^{-1}. The

0022–2461 © *1992 Chapman & Hall*

gas formed was collected with an automatic gas sampler at intervals of 30 min and analysed using argon as the carrier gas.

3. Results

Fig. 1 shows the dimensional changes of the compacts occurring during cyclic heating. The compact of the raw coke powder ground for 15 min shows a large expansion in both directions, parallel and perpendicular to the compression pressure (Fig. 1a, b). The expansion was maintained after the compact was cooled to 50 °C. In this case, such an irreversible expansion as puffing, occurs at low temperatures below 400 °C. On the other hand, the compact of powder ground for 44 h shows relatively small puffing in the direction parallel to the compression pressure, and conversely a small shrinkage in the perpendicular direction, even during the first step of heating (Fig. 1c, d).

From a temperature around 400 °C, both of these compacts start to shrink gradually, and show a maximum rate of shrinkage around 700 °C, which can be mainly attributed to contraction of the constituent coke grains caused by carbonization.

Both compacts show a considerable difference in puffing degree between the directions parallel and perpendicular to the compression. This reflects anisotropic residual strain in the compacts accumulated during the compression process. Fig. 2 shows the dimensional changes of the green compacts with the time elapsed immediately after removal from a die. Both of the compacts show a gradual expansion in the direction parallel to the compression pressure. On the other hand, those in the perpendicular direction are relatively small; expansion of the compact of powder ground for 15 min and shrinkage of that ground for 44 h. These results show that the sample ground for 44 h possesses a better ability to be compacted than does that ground for 15 min, although their packing densities are almost the same, 85%.

As it is evident from Fig. 1, a large shrinkage observed for the compacts around 700 °C suggests a marked contraction of the coke grains due to carbonization, not their sintering. Fig. 3 shows the changes in pore volume, the total amount of closed and open pores in the compacts with calcination temperature. Up to 400 °C the pore volume increases slightly for all samples. This is caused by puffing of the compacts as mentioned above. Above 400 °C the compact of the powder ground for 44 h shows a decrease in pore volume at two different temperatures. A large decrease between 400 and 500 °C is greatly suppressed

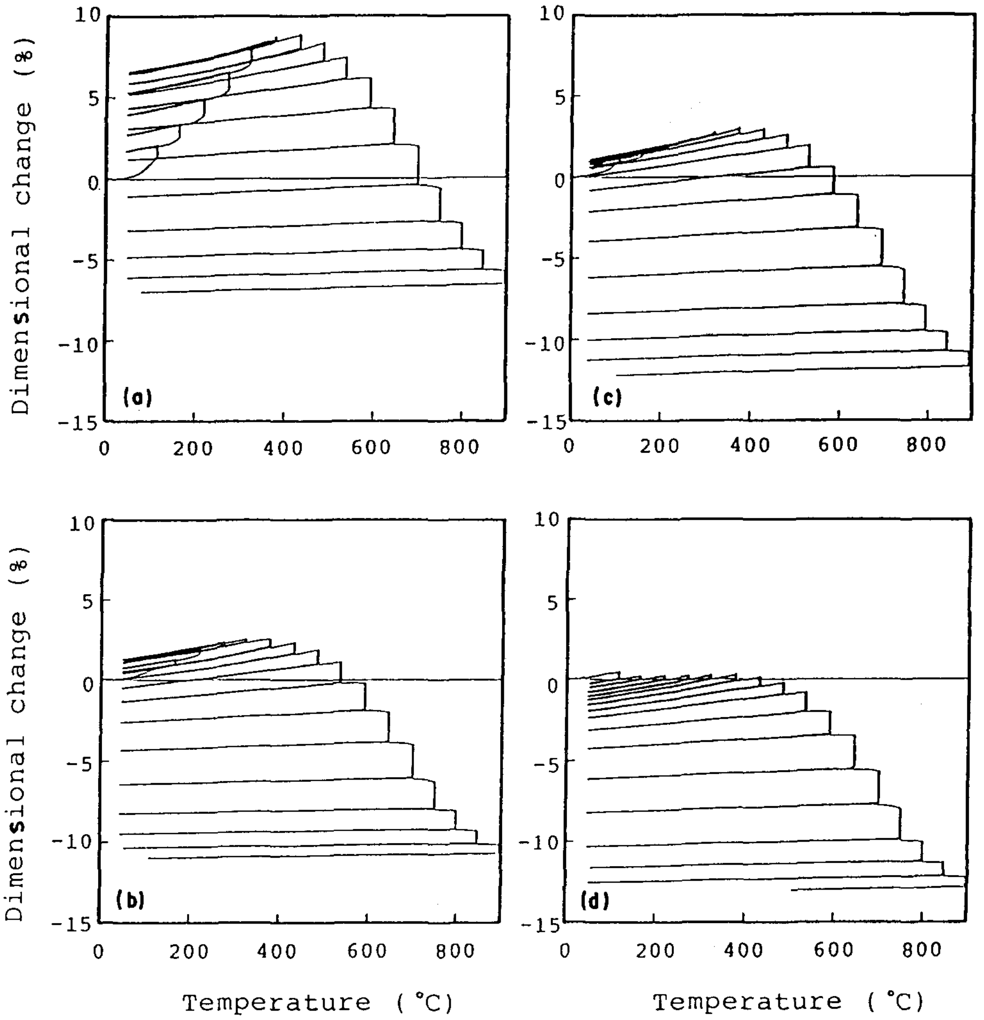

Figure 1 Dimensional changes during cyclic heating of the compacts: (a) parallel direction to the compacting pressure for raw coke ground for 15 min, (b) perpendicular direction for raw coke ground for 15 min, (c) parallel direction for raw coke ground for 44 h, (d) perpendicular direction for raw coke ground for 44 h.

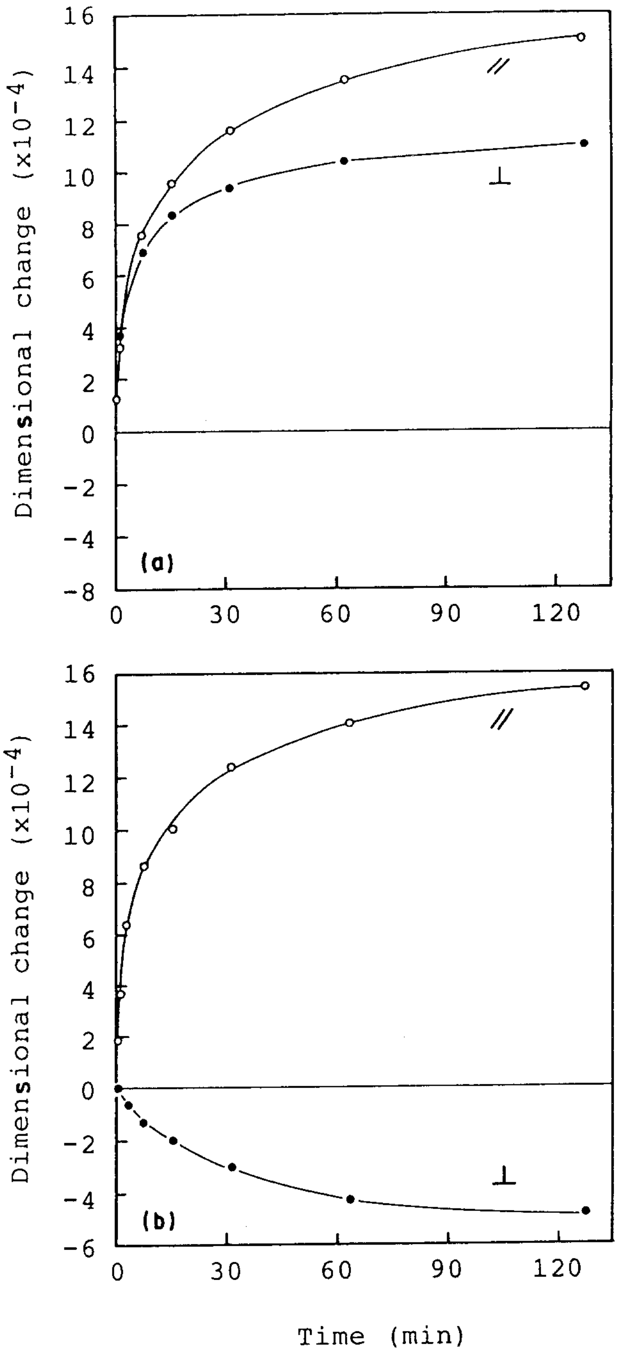

Figure 2 Dimensional changes after compression of the raw coke powders ground for (a) 15 min, (b) 44 h. // and ⊥ indicate directions parallel and perpendicular to the compression pressure, respectively.

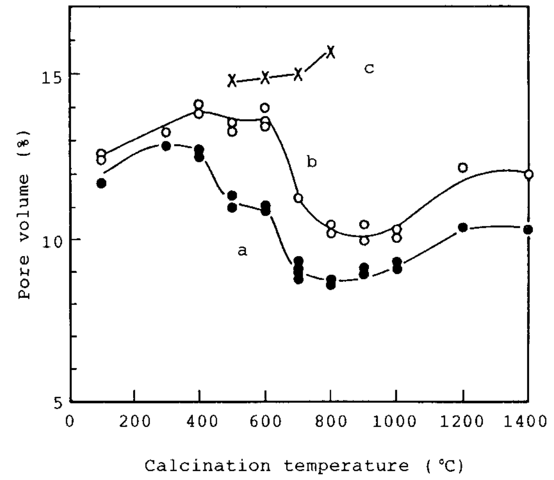

Figure 3 Changes in pore volume in the compact with calcination temperature: (a) ground for 44 h, (b) quinoline-treated after grinding for 44 h, (c) ground for 15 min.

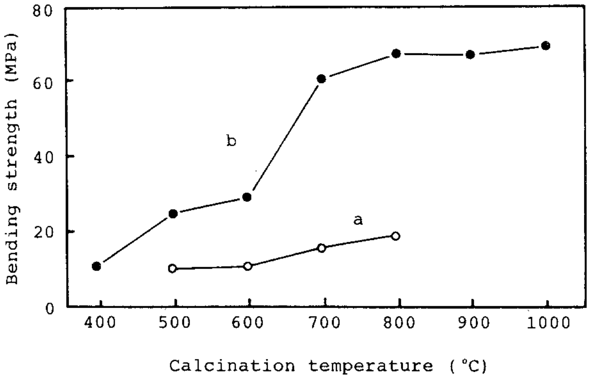

Figure 4 Changes in bending strength with calcination temperature for the compacts of raw coke powders ground for (a) 15 min, (b) 44 h.

when the latter powder is treated with quinoline before compacting. The decrease is found to be closely related to quinoline-soluble components among the coke grains. The decrease between 600 and 700 °C is observed in both compacts of as-ground and quinoline-treated powder. Above 800 °C, a gradual increase in pore volume is observed in both compacts. This increase is considered to be caused by growth of micropores created at 600–800 °C in the constituent coke grains [5]. On the other hand, the compact of the powder ground for 15 min shows no remarkable change in pore volume over the whole range of calcination temperature.

As shown in Fig. 4, a marked increase in bending strength is observed for the sample ground for 44 h, at a calcination temperature of 700 °C. This suggests that bonding between coke grains is strengthened in this temperature range, as expected from the decrease in pore volume shown in Fig. 3. In contrast, the bending strength does not show a very remarkable increase around 600 °C at which the pore volume also decreases, due to the existence of quinoline-soluble components. On the other hand, only a gradual increase in bending strength with calcination temperature is observed for the sample ground for 15 min.

Fig. 5 shows changes in the average size of aromatic carbon layers in the compacts with calcination temperature. We reported previously that the average size of aromatic carbon layers showed almost no remarkable change with grinding, but the stacking number of layers in carbon crystallites decreased with grinding [6]. In the present work, however, the measured average layer size of the sample ground for 44 h, is smaller than that of the sample ground for 15 min. This difference is due to the fact that X-ray measurements in this work were carried out on the compacts formed using a die and plungers, in contrast to those of a previous paper using the powder method. The compacts of powder ground for 15 min are considerably anisotropic, that is, most of the large layers lie in the direction perpendicular to compacting pressure. In contrast to this, the compacts of powder ground for 44 h are isotropic because the grains are round in shape [2]. The X-ray measurements in this work were carried out on a geometrical arrangement in which the diffraction plane was parallel to the compacting pressure direction of the compacts. Thus the measured average layer size of the sample ground for 15 min is larger than that of the sample ground for 44 h. At calcination temperatures below 600 °C, the measured values of average layer size remain almost constant for both samples. Above 600 °C, the size of the carbon layers begins to increase with calcination temperature up to 800 °C.

Fig. 6 shows a comparison of changes in the formation rate of methane with calcination temperature. In the powder ground for 15 min, the formation rate shows a peak at about 600 °C with a small shoulder near 700 °C. By grinding the powder for 44 h, the formation rate of methane at 600 °C decreases slightly, and the shoulder near 700 °C becomes more distinguishable. This indicates that grinding of the raw coke has some influence on the chemical structure at the edge of carbon layers, and results in a change of the formation rate of methane during carbonization.

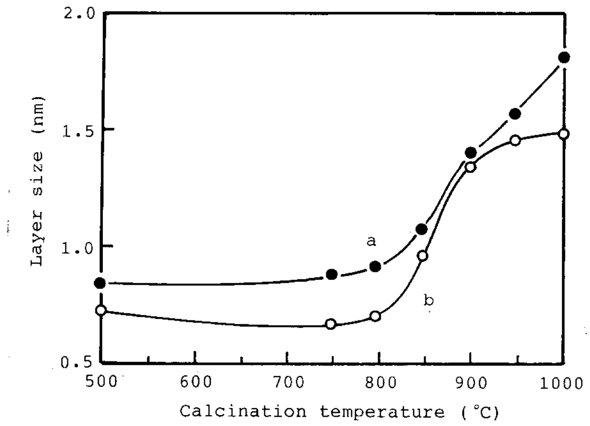

Figure 5 Changes in average layer size with calcination temperature for the compacts of raw coke powders ground for (a) 15 min, (b) 44 h.

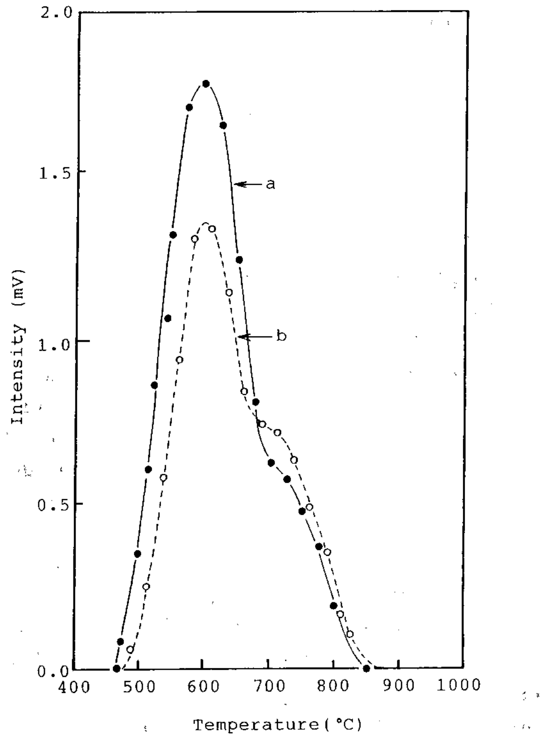

Figure 6 Comparison of the change in formation rate of methane with calcination temperature between the raw coke powders ground for (a) 15 min and (b) 44 h.

Fig. 7 shows the changes in crystallite densities of the ground samples measured by an X-ray diffraction technique. This figure also includes changes in grain and bulk densities and pore volume of the sample ground for 44 h. A gradual increase in bulk density is observed with heat-treatment temperature. Below 2200 °C, the pore volume also shows a slight increase. This increase in bulk density in spite of an increase in pore volume, shows that densification occurs in the compact below 2200 °C due to contraction of constituent grains, rather than sintering between the grains. Above 2200 °C, the density of the grains becomes almost constant. However, the bulk density slightly increases with decreasing pore volume.

4. Discussion

Normally it is very difficult to produce dense carbons from raw cokes by pressureless sintering. This is attributed to large puffing of the powder compact during a calcination process as shown in this work. The puffing of the powder compacts is considered to be induced by breaks of adhesion between grains in the compact. The most reasonable cause for this break is an anisotropic deformation of the grains during calcination. The deformation of the raw coke grains below 500 °C is caused by the thermal expansion and relaxation of residual strains accumulated in the grains during the compacting process. The raw coke before grinding has a large and anisotropic thermal expansion coefficient [7], and probably anisotropic deformation takes place when the residual strains are relaxed by heating because of the anisotropic structure

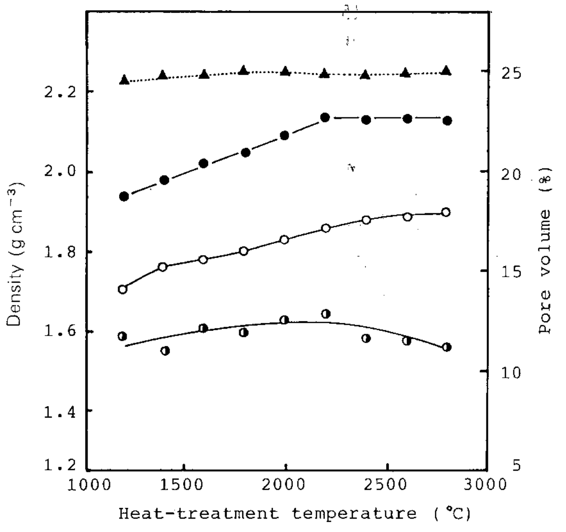

Figure 7 Changes with high-temperature treatment of (○) bulk and (◑) pore volume of the solid, and the densities of the (●) constituent grains and (▲) crystallites for the raw coke ground for 44 h.

of the grains. For the compact subjected to short grinding, the anisotropic deformation of grains during calcination seems to induce breaks in the adhesion between the grains and large puffing of the compact.

On the other hand, a long grinding alters the coke grains into round aggregates with an average size of 10 μm, which consist of few primary grains with a small amount of quinoline soluble components playing the role of binder material [2], and also the anisotropic structure into considerable disordered one [6]. These aggregates are considered to show an isotropic thermal expansion and relaxation of residual strains. This seems to be the reason why the compact showed relatively small puffing during calcination when the powder was subjected to long grinding.

For the compact subjected to long grinding, the decrease in pore volume occurred in two different regions. The first decrease around 500 °C can be related to the existence of quinoline soluble components among the grains. It seems likely that liquid-phase-like sintering, that is, softening of the components and rearrangement of grains to give the most efficient packing, somewhat take place. The second decrease around 700 °C implies densification by sintering of the coke grains. The sintering at this temperature strengthens the bond between the grains, as is inferred from a marked increase in bending strength of the compact. We can consider an evaporation–condensation sintering mechanism [8] in the neck area between the grains, because the raw coke evolves a certain amount of hydrocarbon gases during carbonization. However, the pore volume of the compact does not decrease in this sintering mechanism. The decrease in pore volume around 700 °C, therefore, shows that solid-state sintering also take place, which is due to solid state material transfer of carbon layers and/or low molecular weight components in the raw coke by some mechanism such as diffusion, plastic deformation and viscous flow.

The formation rate of methane reaches a maximum around 600 °C for both compacts, and shows a shoulder near 700 °C which becomes distinguishable on prolonged grinding. It is found in Fig. 3 that the pore volume in the compact decreases at almost the same temperature as the shoulder. A marked growth in the carbon layers is also observed around 700 °C. These facts suggest that there may be some correlation between sintering, growth of the carbon layers and methane formation at this temperature range. The methane formation should take place at the edge of the carbon layers, and it is considered to be somewhat related to growth of the layers and an increase in mobility. It seems likely that the grinding has some effect on the promotion of sintering of the raw coke, by affecting the chemical structure between the carbon layers which results in an increase in the mobility of the layers during calcination around 700 °C.

The grinding of the raw coke results in an increase in oxygen content [1]. Gas analysis showed that the oxygen atoms were removed as CO and CO_2 in the temperature range 450–800 °C. Both of the formation rates of these gases showed a gentle slope as a function of calcination temperature. From this fact, it seems likely that the removal of oxygen atoms during calcination is not closely related to a decrease in pore volume observed at 600–700 °C.

On heat treatment up to 2200 °C, no decrease in pore volume was observed. The densification of the compact was found to be due to contraction of constituent grains. This seems to be caused by a decrease in closed micropores in the grains. A slight increase in pore volume in the compact shows that some of the closed micropores change to open pores, probably hair cracks, in the grains.

The change in density of the grains with heat-treatment temperature was clearly different in the temperature ranges below and above 2200 °C. Above 2200 °C, the density of the grains maintained a constant value, and the pore volume in the compact decreased slightly, in contrast to an increase at temperatures below 2200 °C. These changes at 2200 °C suggest that the densification mechanism of the compact changes in this temperature range, and also there may be some correlation between densification and graphitization, because the graphitization mechanism also changes in this temperature range, that is, the change from a mechanism of smoothing of wrinkles (dewrinkling) in the carbon layers, proposed by Inagaki [9], to material transport through self diffusion, proposed by Fischbach [10]. It seems likely that densification above 2200 °C is related to the latter mechanism. However, the degree of densification above 2200 °C is very small, compared with the densification during the calcination process.

From the grinding effects on densification of the raw coke mentioned above, we can conclude that the suppression of puffing during calcination is the most important factor resulting in the densification of the present carbon compacts. This is caused by the round aggregates of the coke grains produced by a prolonged grinding.

Acknowledgement

The authors thank Dr M. Nakamizo for his help in the preparation of this paper and the many useful suggestions for its improvement.

References

1. I. OGAWA, H. YOSHIDA and K. KOBAYASHI, *J. Mater. Sci.* **16** (1981) 2181.
2. *Idem., Carbon* **23** (1985) 79.
3. I. OGAWA, K. KOBAYASHI and S. NISHIKAWA, *J. Mater. Sci.* **23** (1988) 1363.
4. R. DIAMOND, *Acta. Crystallogr.* **11** (1958) 129.
5. S. MIURA and P. L. SILVESTON, *Carbon* **18** (1980) 93.
6. I. OGAWA and K. KOBAYASHI, *TANSO* (120) (1985) 28.
7. R. W. WALLOUCH and F. V. FAIR, *Carbon* **18** (1980) 147.
8. W. D. KINGERY, "Introduction to Ceramics" (Wiley, New York, London, Sydney, 1960) p. 369.
9. M. INAGAKI, *J. Appl. Crystallogr.* **5** (1972) 295.
10. D. B. FISCHBACH, "Chemistry and Physics of Carbon", Vol. 7 (Marcel Dekker, Inc., New York, 1971) p. 1.

Received 3 September 1990
and accepted 28 February 1991