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Kawasaki Steel's new carbon powder, KMFC (Kawasaki mesophase fine carbon) is produced from mesophase spherules formed by heat-treating pitch. KMFC has out-standing self-sinterability to produce isotropic carbon blocks of high density and strength without any extra binder components. In the present study, changes in the physical properties of KMFC compacts during the sintering process were examined in order to determine the sintering mechanism of a KMFC green compact. The high densification and high strength of KMFC compacts result from the large reduction in pore volume due to the fusion of KMFC at 400-600°C, and from the large shrinkage of the compact over 600°C. Light fractions such as HS (hexane-soluble) components, AS (acetone-soluble) components, and TMO (tar middle oil) play an important role in achieving this high densification and high strength by governing the fusibility of KMFC particles at 400-600°C for their subsequent adhesion.

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A Sintering Mechanism of KMFC Green Compact for High Density Carbon Blocks*



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1 Introduction

Carbon blocks have such useful properties as high conductivity of electricity and heat, high stability up to about 3 000°C under a nonoxidizing atmosphere, high strength at high temperature, high mechanical workability, and self-wettability, with useful applications in chemistry, machinery, electricity, metallurgy, nuclear reactors and so on. With the further development of industrial technology, isotropic carbon blocks of even higher density and higher strength are demanded.

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Kawasaki Steel's new carbon powder, KMFC (Kawasaki mesophase fine carbon) is produced from mesophase spherules formed by heat-treating pitch. KMFC has outstanding self-sinterability to produce isotropic carbon blocks of high density and strength without any extra binder components.

In the present study, changes in the physical properties of KMFC compacts during the sintering process were examined in order to determine the sintering mechanism of a KMFC green compact. The high densification and high strength of KMFC compacts result from the large reduction in pore volume due to the fusion of KMFC at 400–600°C, and from the large shrinkage of the compact over 600°C. Light fractions such as HS (hexane-soluble) components, AS (acetone-soluble) components, and TMO (tar middle oil) play an important role in achieving this high densification and high strength by governing the fusibility of KMFC particles at 400–600°C for their subsequent adhesion.

Table 1 Physical properties of graphite block³⁾ made from a typical KMFC

Bulk density	(g/cm ³)	1.90
Shore hardness		85
Bending strength	(MPa)	98
Electrical resistivity	(μΩ·cm)	1 400
Compressive strength	(MPa)	181
Anisotropic ratio of thermal expansion coefficient		1.01

³⁾ Forming pressure: 54 MPa
Graphitizing: 2 500°C × 2 h

coal tar pitches.⁶⁻⁸⁾ KMFC has high self-sinterability for producing isotropic carbon blocks of high density and strength without any extra binder components by forming, baking, and if necessary, graphitizing steps, as shown in **Table 1**.^{9,10)}

The manufacturing process for KMFC shown in **Fig. 1** comprises four main steps, using coal tar pitch as the raw material: (1) heat-treatment, (2) solvent-extraction

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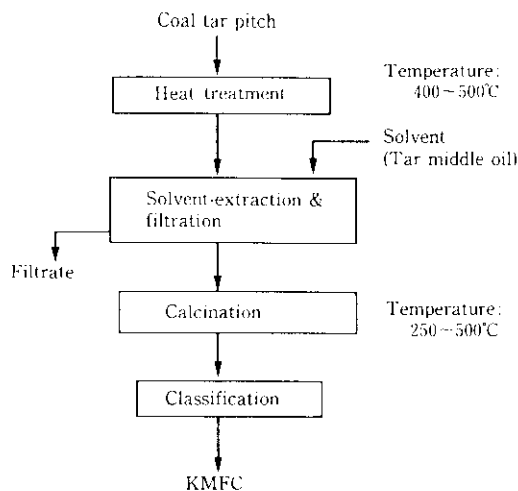


Fig. 1 Manufacturing process for KMFC powder

and filtration, (3) drying and calcination, and (4) classification. One of the keys to this process has proved to be the solvent-extraction step that leaves β -resin (benzene-insoluble and quinoline-soluble component) in the mesophase spherules as a binder by using tar middle oil as solvent. The other key is the calcination step for removing the remaining solvent and for adjusting the sinterability of KMFC by thermally polymerizing the β -resin.¹¹⁾

In the present study, changes in physical properties of KMFC compacts during the sintering process between room temperature and 1000°C were examined in order to determine the sintering mechanism of a KMFC green compact. The influence of the light oil fractions contained in KMFC and the heating rate on the sinterability of KMFC were also examined.

2 Experimental

2.1 Preparation of the KMFC Samples

Approximate analyses of the KMFC samples used in the study are shown in Table 2. Samples A, B and C were produced in the commercial KMFC plant in the

Table 2 Properties of KMFC used in this study (wt%)

Sample ^{a)}	TI ^{b)}	QI ^{c)}	VM ^{d)}	Ash
A	97.5	95.5	8.6	0.36
A-HI	98.0	96.4	8.2	—
B	97.4	92.7	9.0	0.32
B-AI	98.0	93.5	8.8	—
C	96.8	95.0	9.1	0.36
C-TMO	95.7	94.0	10.2	—

^{a)} A, B, C: Produced by the KMFC-commercial plant

A-HI: Hexane insoluble component of A

B-AI: Acetone insoluble component of B

C-TMO: Obtained from C by kneading tar middle oil of 2wt%

^{b)} TI: Toluene insoluble

^{c)} QI: Quinoline insoluble

^{d)} VM: Volatile matter (weight reduction after leaving at 800°C for 7 min)

Chemical Division of Kawasaki Steel under various operating conditions. A-HI is the hexane-insoluble component of A, and B-AI is the acetone-insoluble component of B, which were both prepared by solvent-extraction. C-TMO was obtained from C by kneading with 2 wt% of tar middle oil (b.p. 125–250°C).

2.2 Forming and Heat Treatment

The experimental procedure is shown in Fig. 2. KMFC samples of 50 g were each formed into a green compact of 50 mm dia. × 20 mm height by cold isostatic pressing (CIP) under a pressure of 54 MPa. The green compacts were heat treated to the specified temperature ranging from 200°C to 1000°C with heating rates of 10.4 or 5.2°C/h in coke breeze.

2.3 Measurement of the Physical Properties and Analysis of the Fine Structure

A thermogravimetric(TG) analysis of the KMFC samples was conducted by using a Shimadzu DT-40 thermal analysis system. The measurement conditions were as follows: sample weight, 200 mg; heating rate, 10°C/min; maximum temperature, 1000°C and nitro-

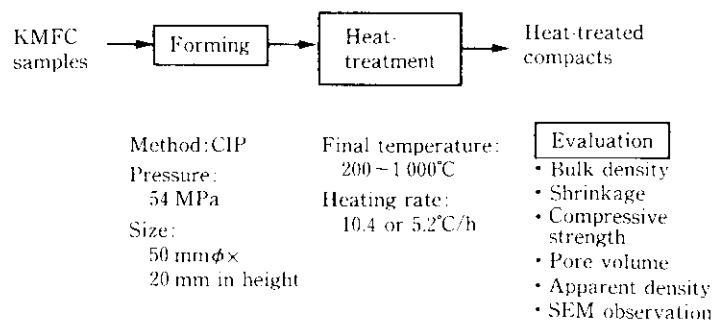


Fig. 2 Experimental procedure

gen atmosphere flow rate, 100 ml/min.

The physical properties of the green and heat-treated compacts were evaluated by measuring the bulk density, dimensional shrinkage, and compressive strength. The bulk density of the compacts was obtained by the underwater specific gravity measurement. A Shimadzu AGS-500A autograph was used to measure the compressive strength, the sample size being 100 mmL × 10 mmW × 10 mmH. The dimensional shrinkage ($\Delta L/L$) of the compacts during the sintering process was calculated from the following equation:

$$\Delta L/L = \frac{(D_0 - D_b)}{D_0} \times 100 \dots\dots\dots(1)$$

where D_0 is the diameter of the green compact, and D_b is the diameter of the heat-treated compact.

To analyze the fine structure, the crushed face of the heat-treated compact was observed with a scanning electron microscope (SEM), and the pore volume of the compact was measured with a Mercury Porosimeter pore sizer 9300 made by Micrometric. The distribution of pore size was measured in the range from 0.001 μm to 1 μm . Apparent density was calculated from the following equation:

$$AD = \frac{BD}{(100 - P_0)} \times 100 \dots\dots\dots(2)$$

where AD is the apparent density, BD the bulk density, and P_0 the pore volume.

3 Results

3.1 Changes in the Physical Properties and Fine Structure of KMFC Compacts during the Sintering Process

The changes in bulk density and dimensional shrinkage of the KMFC compacts of sample A during the sintering process are shown in Fig. 3. At temperatures below 400°C, the dimensional shrinkage was only 0.5%, and no increase in bulk density was apparent. On the other hand, at temperatures from 400°C to 1000°C, increases in dimensional shrinkage and bulk density of the compact were clearly observed with increasing heat-treatment temperature.

The changes in compressive strength are represented in Fig. 4. At temperatures below 400°C, the compressive strength of the heat-treated compact was nearly equal to that of the green compact, showing that the strength of the compact wasn't improved by heat treating less than 400°C. At temperatures over 400°C, the compressive strength was increased with increasing temperature.

Changes in the pore volume during the sintering process are shown in Fig. 5. Only a small increase in pore volume from 16.2% to 17.6% was observed with increasing temperature up to 400°C. However, the pore volume markedly decreased between 400°C and 600°C,

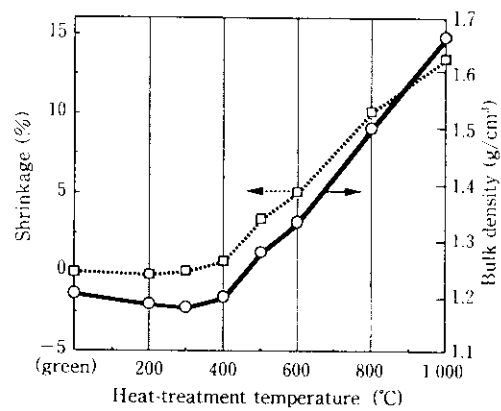


Fig. 3 Change in bulk density and shrinkage of A-compacts during sintering process (Heating rate: 10.4°C/h)

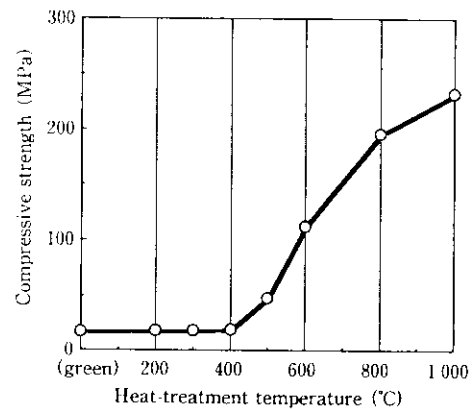


Fig. 4 Change in compressive strength of A-compacts during sintering process (Heating rate: 10.4°C/h)

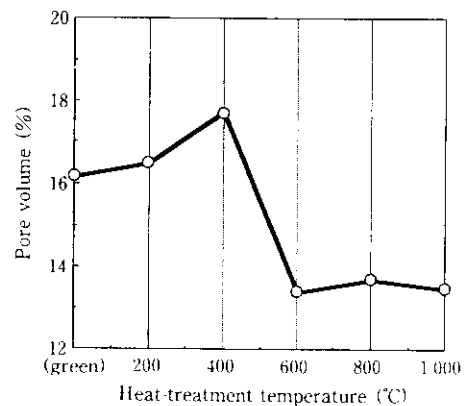


Fig. 5 Change in pore volume of A-compacts during sintering process (Heating rate: 10.4°C/h)

although it remained constant at temperatures over 600°C.

The change in apparent density, calculated from the bulk density and pore volume, is presented in Fig. 6. The apparent density increased at temperatures over

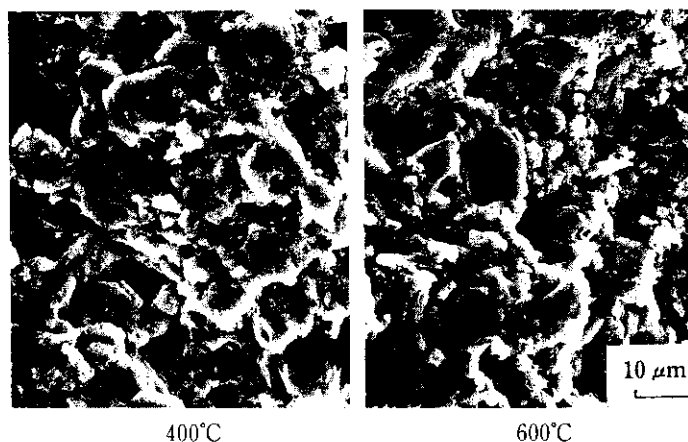


Photo 1 SEM photographs of heat-treated A-compacts (Heating rate: 10.4°C/h)

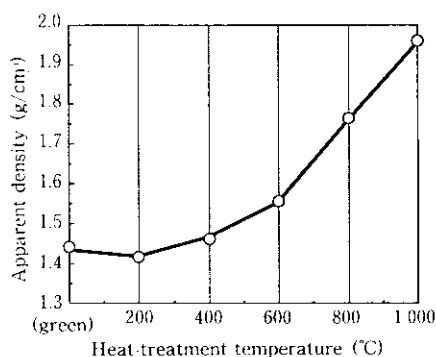


Fig. 6 Change in apparent density of A-compacts during sintering process (Heating rate: 10.4°C/h)

400°C with increasing heat-treatment temperature. Particularly at temperatures over 600°C, the apparent density, increased sharply, although it showed little increase between 400°C and 600°C.

SEM photographs of the crushed face of sample A compacts heat-treated at 400°C and 600°C are shown in Photo 1. The spherical KMFC particles can be clearly observed in the compact heat-treated at 400°C. However, in the case of the compact heat-treated at 600°C, the spherical particles have disappeared and destroyed particles can be seen. This observation of the compact heat-treated at 600°C clearly shows fusion and adhesion at the surface of KMFC particles. This result is also supported by the changes in pore volume shown in Fig. 5. Namely, the decrease in pore volume between 400°C and 600°C is thought to be due to fusion and adhesion of the KMFC particles.

3.2 Influence of Light Oil Fractions on the Sinterability of KMFC

TG profiles of the KMFC A-HI and C-TMO samples are shown in Fig. 7, in comparison with samples A and C, respectively. The weight loss rate of A-HI is clearly

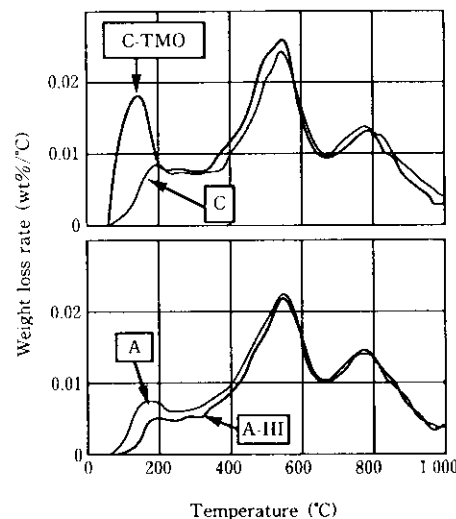


Fig. 7 TG-profiles of KMFC

less than that of A at temperatures below 400°C. C-TMO has a significantly larger weight loss rate than that of C at temperatures below 200°C. These results indicate that the major hexane-soluble component and tar middle oil used as solvents for extraction in producing KMFC evolve at the early stage of the sintering process.

Figure 8 illustrates the influence of the light oil fractions on the bulk density and shrinkage of compacts heat-treated at 1000°C. The bulk density and shrinkage of the heat-treated A-HI and B-AI compacts are smaller than those of the heat-treated A and B compacts, respectively. Conversely, the bulk density and shrinkage of the heat-treated C-TMO compact are larger than those of the heat-treated C compact. These results clearly show that the light oil fractions of HS, AS and TMO are strongly related to the sinterability of KMFC. B-AI suffered from a larger decrease in bulk density of its resulting compact than A-HI did. The solubility of acetone for pitches is greater than that of hexane, and

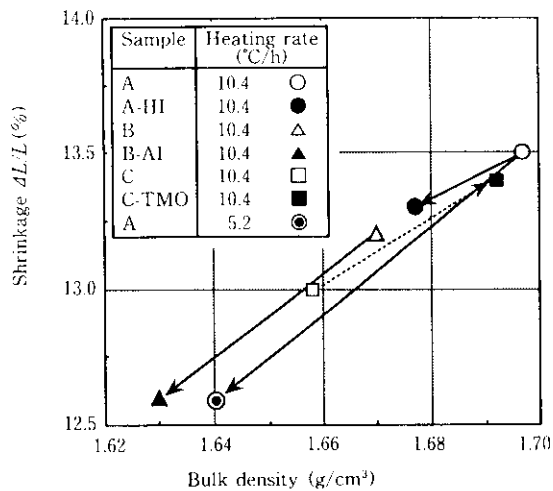


Fig. 8 Influence of light oil fractions and heating rate on bulk density and shrinkage of heat-treated compacts at 1000°C

the light oil fractions of the B-AI sample were removed much more than those of the A-HI sample. The influence of the AS-HI fraction (acetone-soluble and hexane-insoluble component) on the sinterability of the KMFC compact is also apparent.

3.3 Influence of Heating Rate on the Sinterability of KMFC

The influence of heating rate on the bulk density and shrinkage of compact A heat-treated at 1000°C is shown in Fig. 8. A heating rate of 5.2°C/h provided a lower bulk density and shrinkage than that of 10.4°C/h. The heating rate is also relevant to the sinterability of a KMFC compact.

4 Discussion

The sintering of KMFC green compacts is considered to progress in two temperature ranges: one from 400°C to 600°C and the other over 600°C. At temperatures between 400°C and 600°C, sintering in the liquid phase

proceeds and particles adhere through fusion of a binder component around the mesophase spherules which remains from the extraction process. At temperatures above 600°C, hexagonal layers of carbon and graphite are developed and closely packed in the solid phase, so that further densification of the compacts is achieved. Our results showing a decrease in porosity between 400°C and 600°C (Fig. 5), and a sharp rise in apparent density over 600°C (Fig. 6), verify this. Liquid-phase sintering promotes adhesion between the particles by removing macropores at the interfaces of the particles. This adhesion results in an increase in both the bulk density and strength of the compact. At the same time, some hydrocarbons are liberated from the compacts, leaving micropores within the compacts. Sintering in the solid phase at temperatures over 600°C is considered to have brought about the increase in bulk density through an increase in the apparent density. Macropores would never be removed when the fusion of a binder component is insufficient, even if significant shrinkage occurs at temperatures over 600°C. The sinterability between 400°C and 600°C by fusion with a binder component seems to govern the properties of the ultimate carbon product. Figure 9 shows an inferred sintering mechanism of KMFC green compacts based on the foregoing hypothesis.

The extent of sintering in the liquid phase by fusion with a binder component between 400°C and 600°C is strongly influenced by the amount and quality of the volatile fraction and heating rate. It was found that such volatile fractions as the hexane-soluble component and acetone-soluble component in the KMFC particles or tar middle oil that was used in the extraction process had strong influence on both the shrinkage and bulk density of the compacts, although the greatest effect was at temperatures below 400°C. It is considered that the diffusion rate of these volatile fractions was slow inside the compact during the sintering process, and a portion of the volatile fractions remained in the compact between 400°C and 600°C. Consequently, the volatile fractions are considered to contribute to the increase in bulk density of the compacts, thus promoting fusion

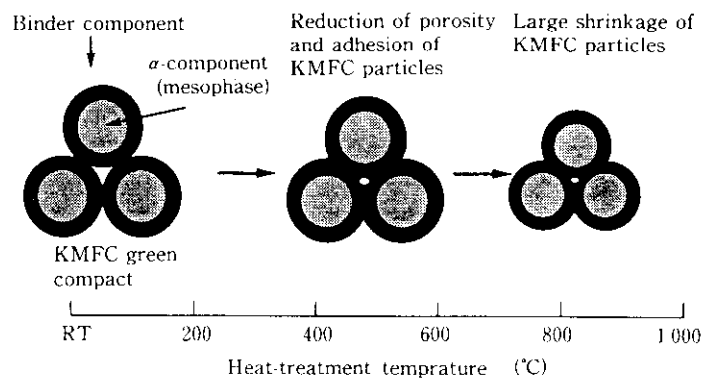


Fig. 9 A model of the sintering mechanism of KMFC green compact

with the binder component in the KMFC particles.

The influence of heating rate on the degree of fusion has been reported for coal.¹²⁻¹⁴ Mochida and co-workers have reported that a rapid heating rate shifted the evolution point for volatile matter to a higher temperature, and that the influence of this volatile matter became more significant to carbonization. Therefore, the fusibility of coke was improved.

During the sintering process for the KMFC compacts, the higher heating rate of 10.4°C/h allowed greater participation by the volatile fractions than the heating rate of 5.2°C/h by retarded evolution. This result also suggests that the volatile fraction in KMFC would play an important role in the sinterability of the particles.

From this study, it is concluded very important for the quality-control of KMFC not only to control the level of aromaticity of the β -resin which acts as a binder in the compact, but also to adjust the amount and composition of the volatile fractions in KMFC.

5 Conclusions

The influence of the volatile fractions and heating rate on the sinterability and physical properties of KMFC compacts during the sintering process at temperatures between room temperature and 1 000°C were investigated, and the following conclusions have been obtained about the high density sintering mechanism KMFC green compacts.

(1) High densification and high strength of KMFC compacts result from the large reduction of macropores due to fusion and adhesion of the KMFC particles between 400°C and 600°C (sintering in the liquid phase) and to the large shrinkage of the compact above 600°C (sintering in the solid phase).

(2) The light fractions such as HS, AS and TMO play an important role in achieving the high densification and high strength of the KMFC compact by governing the fusibility of the binder component in KMFC particles between 400°C and 600°C.

(3) Rapid heating accomplishes high densification of the KMFC compact as it promotes fusion due to the retarded volatilization from the KMFC compact.

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