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Manufacturing Processes and Characteristics of KMFC Powder and KMFC Graphite Blocks*

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1 Introduction

Recently, demands have been increasing for upgrading quality of graphite blocks and reducing their manufacturing processes. To satisfy these demands, the authors have successfully developed a new carbon powder, **KMFC** (Kawasaki Mesophase Fine Carbon), producible into isotropic graphite blocks having high density and strength by using mesophase spherules formed under heat-treatment of pitches. In 1987, a KMFC commercial plant of 30 t/month was constructed at Chiba Plant of Chemical Division, to start regular production and sales of KMFC powder.

This paper describes background of KMFC powder development, manufacturing processes and characteristics of KMFC powder, and characteristics of graphite blocks made from KMFC powder.

2 General Background

2.1 Description of Conventional Method for Manufacturing Graphite Blocks

Graphite blocks have a variety of useful properties, including high conductivity of electricity and heat, high stability up to 3000°C under a nonoxidizing atmosphere, high strength at high temperatures, high erosion resistance against chemicals, high mechanical workability and high self-wettability. Therefore, graphite blocks are widely used in various fields: As electrodes for use in electrochemistry; as crucibles, boats and the like for use in metallurgy; and as mechanical seals for machines.

These graphite blocks are generally produced by mixing and kneading pulverized filler coke with a binder, forming the mixture into a green shaped body, which is subjected to sintering and graphitizing. However, it is difficult to produce graphite blocks having high density and strength, because not only the filler coke itself is porous, but these binder such as coal tar pitch, synthetic resin and the like generate a large number of voids during the sintering process because of their large quantity of volatile matter. Moreover, complicated operational processes are required when mixing the filler coke with the binder, and the operating environment is unhealthy. To attain high density and strength of graphite blocks, pitch impregnation and rebaking of the sintered blocks are often repeated, and yet the resultant graphite blocks have a density as low as about 1.8 g/cm³ and a maximum bending strength of 600 kg/cm². Furthermore, the resultant graphite blocks generally have anisotropic physical properties due to the anisotropy of needle-like filler coke, making it difficult to produce isotropic graphite

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blocks. However, with broadening applicable fields of graphite blocks brought by the advances in manufacturing technology, the requirements for isotropic graphite blocks having high density and strength are rapidly increasing.

2.2 Formation and Application of Mesophase Spherules

Various attempts have been made in order to produce isotropic graphite blocks having high density and strength. One such attempt, employing mesophase spherules, was developed by Y. Yamada and H. Honda, et al.[1,2] in the National Industrial Research Institute of Kyushu Japan. Mesophase spherules generated under heat-treatment of pitches at 350~500°C, are optically anisotropic spherules with a diameter under 50 μm.[3,4] An optical micrograph of mesophase spherules generated into the pitch matrix is shown in **Photo 1**. The mesophase spherules have a lamella structure, which is stacked by high molecular aromatics, similar to that of graphite as shown in **Fig. 1**, and are called graphite or coke precursor. Yamada et al.[1,2] discovered that the mesophase spherules completely separated from the pitch matrix by extraction with a strong solvent to pitches such as quinoline can be directly transformed into high density and strength graphite blocks without requiring any binder during forming, sintering and graphitizing. Furthermore, the mosophase spherules' spherical shape serves to arrange themselves randomly on forming. The random arrangement of them provides graphite block with isotropic physical properties in spite of the anisotropic structure of the mesophase spherules.

However, since the sinterability of the mesophase spherules produced by Yamada's method is weak, it is difficult to stably transform them into isotropic graphite blocks having high density and strength for industrial materials.

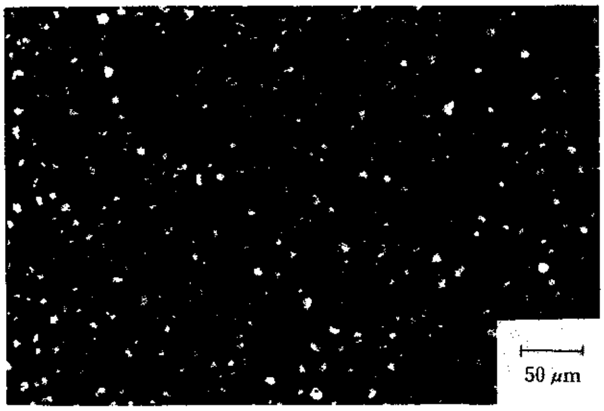


Photo 1 Optical micrograph of mesophase spherules generated in pitch matrix

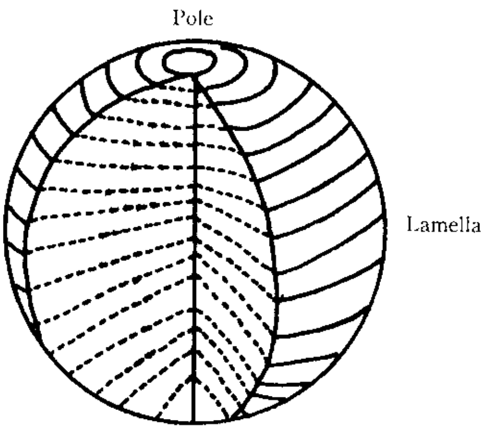


Fig. 1 Structure model of mesophase spherule

3 Manufacturing Process for Producing KMFC Powder

KMFC is a new carbon powder produced by the largely improved Yamadas' method.[1,2] The manufacturing process for KMFC powder developed by the original technology of Kawasaki Steel Corporation is shown in **Fig. 2**[5]. The manufacturing process comprises four main steps using coal tar pitch as a raw material; (1) heat-treatment, (2) solvent-extraction and filtration, (3) drying and calcination, and (4) classification.

Coal tar pitch is heat-treated at 400~500°C in order to nucleate and grow the mesophase spherules in the heat-treatment step. Particle size of the mesophase spherules and resin constitution of the heat-treated pitch are controlled by varying the heat-treating conditions and the quality of the raw coal tar pitch.

In the solvent-extraction and filtration step, the mesophase spherules generated into the heat-treated pitch are separated from the pitch matrix. The mesophase spherules are coated with β-resin (benzene-insoluble and quinoline-soluble component) by using a tar middle oil as a solvent. The β-resin is a heavy component of the pitch

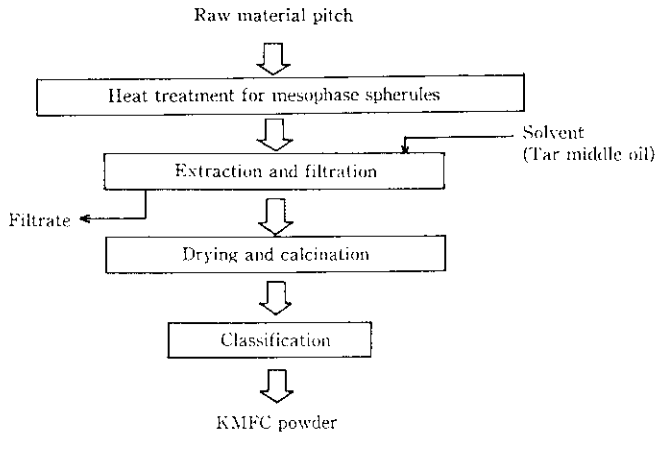


Fig. 2 Manufacturing process for producing KMFC powder

and serves as a good binder when the mesophase spherules are applied as raw materials for making graphite blocks.

Drying and calcination treatments are carried out at a temperature of 250~500°C to remove the solvent remaining in the filtration residue and to adjust the sinterability of the mesophase spherules by thermally polymerizing a part of the β-resin into a QI (quinoline-insoluble) component.

The main features of this process lie in the solvent-extraction step for coating the mesophase spherules with the β-resin as a binder and in the calcination step for adjusting the sinterability of the mesophase spherules[6,7].

4 Features and Sintering Mechanism of KMFC Powder

4.1 Features of KMFC Powder

Properties and features of KMFC powder are enumerated below.

(1) Fine Spherical Powder

A particle size distribution and scanning electron micrograph of a typical KMFC powder are shown in

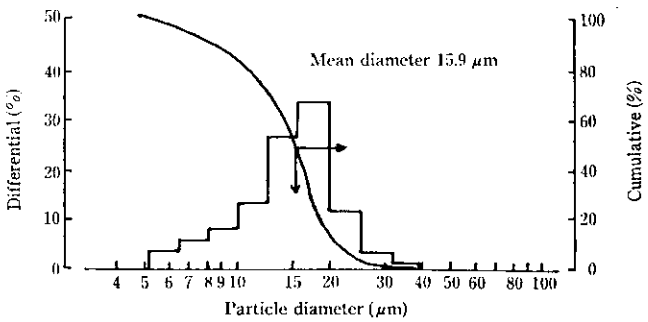


Fig. 3 Particle size distribution of KMFC powder

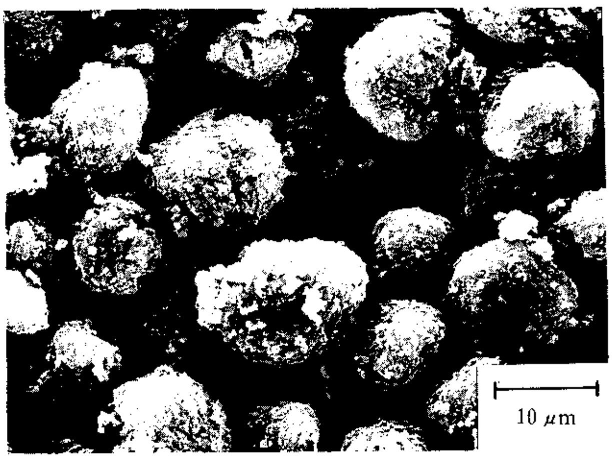


Photo 2 Scanning electron micrograph of KMFC powder

Table 1 Proximate and ultimate analysis values of KMFC powder (wt.%)

Proximate analysis				Ultimate analysis				
BI*	QI**	VM***	Ash	C	H	N	S	O
97.0 ~ 98.0	95.0 ~ 85.0	8.0 ~ 12.0	0.2 ~ 0.1	93.1 ~ 93.5	3.1 ~ 2.9	1.5 ~ 1.0	0.3 ~ 0.2	2.0 ~ 2.4

*BI : Benzene insoluble
**QI : Quinoline insoluble
***VM: Volatile matter (weight reduction after leaving at 800°C for 7 min)

Fig. 3 and Photo 2, respectively. KMFC powder is of spherical shape with an average particle diameter of about 10 to 20 μm.

(2) Excellent Sinterability

Proximate and ultimate analysis values of KMFC powder are shown in **Table 1**. KMFC powder contains hydrogen of about 3 wt.% and has excellent sinterability because of dissolution of the binder component at a temperature of 400~600°C as described below. Therefore, KMFC powder can be processed into high density and high strength graphite blocks without using any extra binder.

(3) Isotropy

Physical structure of KMFC powder itself is anisotropic, similar to graphite; however, formed KMFC compact presents isotropic property since KMFC powder arranges randomly on forming due to its fine spherical shape.

4.2 Sintering Mechanism of Green Compact

The green compact (A, B) shaped from two kinds of KMFC powder, with their sinterability controlled by varying calcination conditions, were sintered in order to determine the sintering mechanism by studying the change in physical properties of the green compact KMFC during the sintering process. The dimensions of the green compacts were 80 mmϕ × 35 mm t, the forming pressure was 550 kg/cm^2 and the heating rate in the sintering process was 10°C/h.

The change in bulk density of the KMFC compacts during sintering is shown in **Fig. 4**. Although A has a higher density than B at 1000°C because of its higher sinterability, both KMFC compacts show a major increase in density at temperatures over 600°C. The difference of the densities of A and B at 1000°C arises from the difference of their densities at about 400°C. Furthermore, the strength of the compacts emerge at a temperature of 400~1000°C (**Fig. 5**). The change in porosity of the KMFC compacts during the sintering process is shown in **Fig. 6**. Although A shows a dramatic reduction in pore volume at a temperature between 400 and 600°C, B's value is nearly constant during the sintering process.

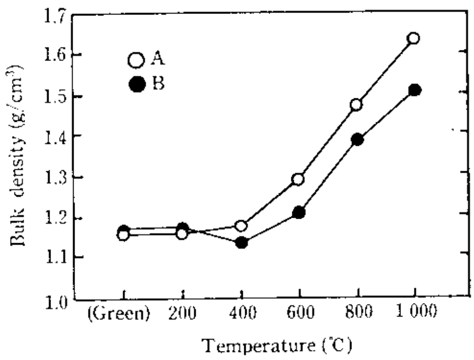


Fig. 4 Change in bulk density of shaped KMFC compact during sintering process

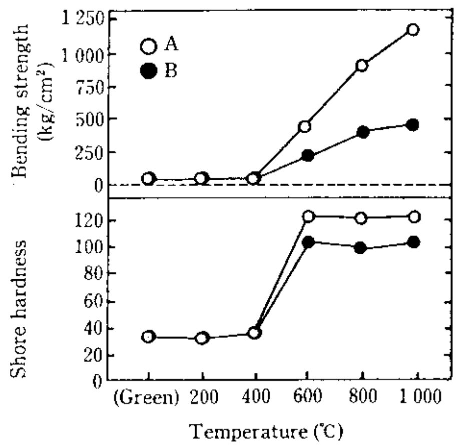


Fig. 5 Change in bending strength and shore hardness of shaped KMFC compact during sintering process

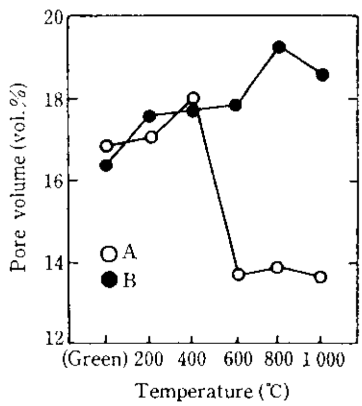


Fig. 6 Change in pore volume of shaped KMFC compact during sintering process

These results suggest that carbonization at a temperature of 400～600℃ plays an important part in high densification and strength of the sintered KMFC body. The sintering mechanism of the KMFC compacts was

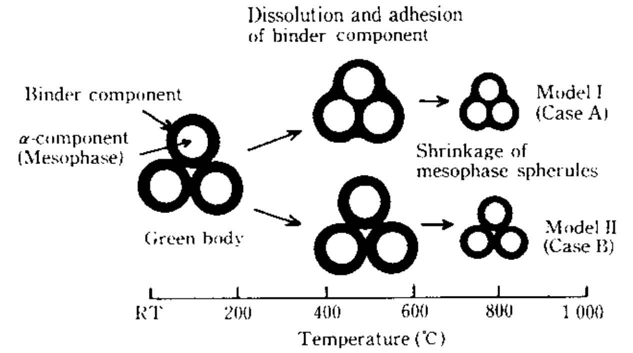


Fig. 7 Sintering model of KMFC

inferred as follows: The high densification and strength of the sintered KMFC body result from adhesion between the mesophase particles and the reduction of porosity, due to carbonization in liquid phase of the QS (quinoline-soluble) component in the mesophase spherules at a temperature between 400 and 600°C. Furthermore, at temperatures greater than 600°C, a large shrinkage of the mesophase spherules themselves becomes a main factor for higher densification and strength of the sintered KMFC body. A model of the sintering mechanism is shown in **Fig. 7**[8].

5 Manufacturing Process and Characteristics of KMFC Graphite Blocks

5.1 Manufacturing Process for Graphite Blocks

The manufacturing process for KMFC graphite blocks, in comparison with the conventional process, is shown in **Fig. 8**. The KMFC method is simpler than the conventional method because the steps of kneading with a binder and of pitch impregnation for attaining high density and strength are not required.

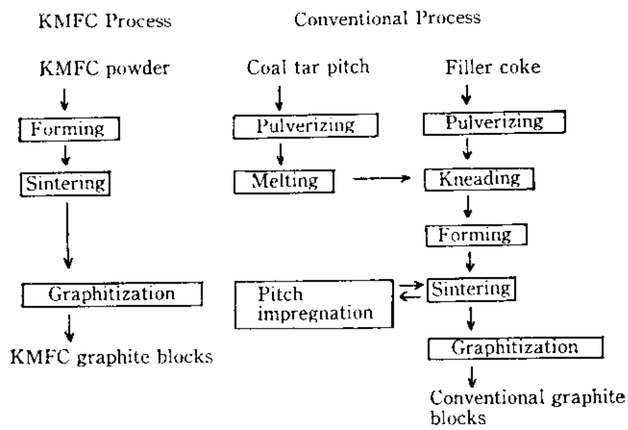


Fig. 8 Processes for producing graphite blocks

5.2 Physical Properties

Physical property values of KMFC graphite blocks, which are graphitized at about 2500°C, are shown in **Table 2**. Results indicate that KMFC graphite blocks have twice the mechanical strength of general isotropic graphite currently available commercially. The anisotropic ratio in the measurement of the thermal expansion coefficient reaches 1.01, indicating almost perfect isotropy. The pore distribution of KMFC graphite blocks is shown in **Fig. 9**. KMFC graphite blocks have a smaller pore radius and pore volume than general isotropic graphite.

Table 2 Physical properties of graphite blocks made from KMFC powder

		KMFC graphite block*	Conventional graphite block
Bulk density	(g/cm^3)	1.90	1.77
Shore hardness		85	54
Bending strength	(kg/cm^2)	1 000	400
Electrical resistivity	($\mu\Omega\cdot$cm)	1 400	800
Compressive strength	(kg/cm^2)	1 850	1 000
Young's modulus	(kg/mm^2)	1 300	1 100
Thermal expansion coeff.	(10^{-6}/°C)	6.0	4.6
Anisotropic ratio to thermal expansion coeff.		1.01	1.14

* Forming pressure 550 kg/cm^2, green block size 100 mmϕ x 35 mm/h, graphitizing 2 500°C x 2 h

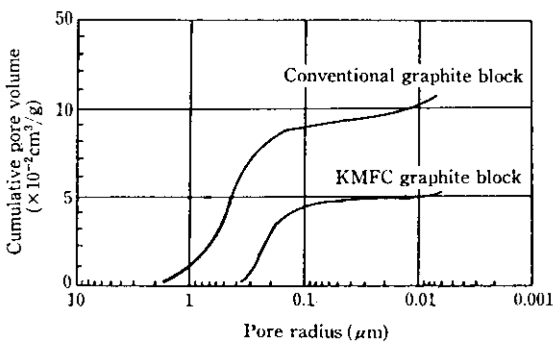


Fig. 9 Pore distribution

5.3 Relationship between Graphitizing Temperature and Physical Properties

An effect of the graphitizing temperature on the physical properties of KMFC graphite blocks is shown in **Fig. 10**. It is clearly observed that with an increase of temperature, there is a significant increase in bulk density, and a decrease in electrical resistivity, although bulk density remains constant at temperatures greater than 2000°C. On the other hand, bending strength reaches a maximum value at around 1600°C. Although graphite blocks are generally graphitized at around 2500°C, the graphitizing temperature for the KMFC blocks should be controlled according to their application because their physical properties strongly depend on the graphitizing temperature as described above.

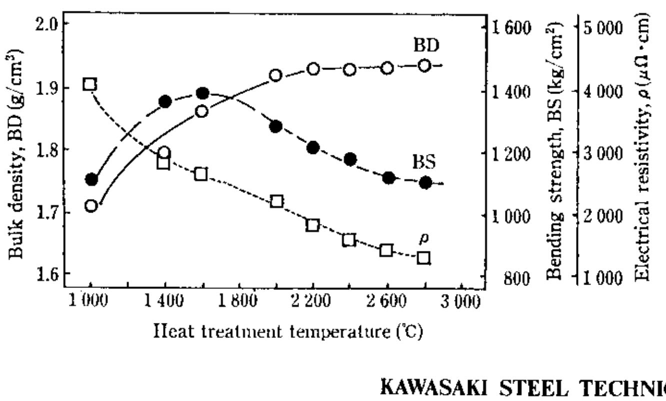
5.4 Major Applications and Characteristics for Practical Use

Major applications of KMFC graphite blocks are as follows:

(1) Electro-Discharge Machining
Electrodes for electro-discharge machining
(2) Metallurgical Use
Jigs, hot press molds, continuous casting nozzles, crucibles, etc.
(3) Machine Use
Bearings, mechanical seals, piston rings, etc.
(4) Nuclear Applications

Because of their superior properties, the application of KMFC graphite blocks has been expanding increasingly in a variety of fields. Their practical application in electro-discharge machining electrodes, which attracts particular attention, is shown in **Fig. 11**. The homogeneous and isotropic structure of KMFC graphite blocks assure precise and rapid machining with a low wear ratio under operating conditions from coarse machining to fine machining. Furthermore, KMFC graphite blocks are easily shaped into very thin plates of 0.05 mm t which can be used as electro-discharge machining electrodes for making deep grooves into hard steel block.

Fig. 10 Effect of heat-treatment temperature on physical properties of KMFC block



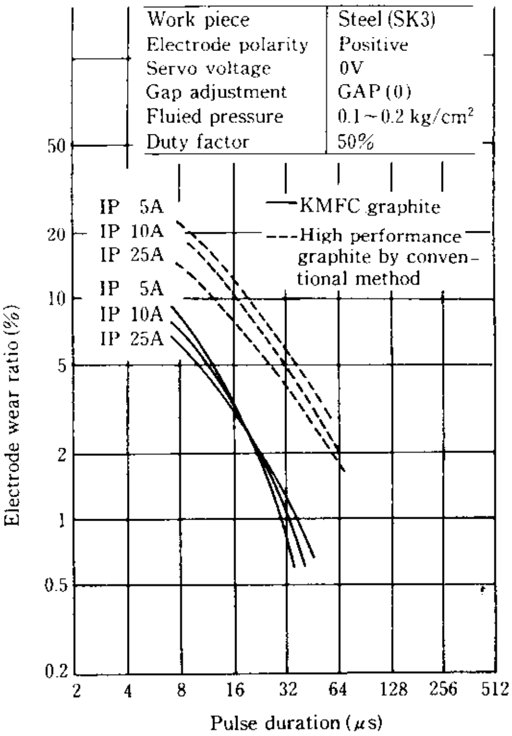


Fig. 11 Comparison of electrode wear ratio in the electro-discharge machinings with KMFC graphite electrode and a conventional graphite electrode

6 Conclusions

The industrial production process for producing a new carbon powder, KMFC, producible into graphite blocks has been successfully developed under original KSC technology. The characteristics of the manufacturing process, KMFC powder and KMFC graphite blocks are as follows:

(1) The manufacturing process for KMFC powder consists of ① heat-treatment, ② solvent-extraction and filtration, ③ drying and calcination, and ④ classification. The main features of this process lie in the solvent-extraction and filtration step for coating the mesophase spherules with the β-resin and the calcination step for adjusting the sinterability of the mesophase spherules by thermal polymerization.

(2) KMFC powder consists of spherules with an average particle diameter of about 10 to 20 μm, and can be directly processed into graphite blocks without using any binder.

(3) The high densification and strength of the sintered KMFC body result from adhesion between the mesophase particles and a porosity reduction, due to dissolution of quinoline-soluble component in KMFC powder at a temperature between 400 and 600°C, and a large shrinkage of the mesophase spherules themselves at temperatures greater than 600°C.

(4) KMFC graphite blocks have a density and a mechanical strength higher than those of any other general graphite blocks and, further, possess an almost perfect isotropy in their physical properties.

KMFC graphite blocks have been developed in order to satisfy the needs of various industrial fields, and are expected to be widely used as an industrial material due to their excellent properties.

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