

# Development of Carbon Blocks for Blast Furnace Hearths

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## Abstract

*Carbon blocks have been used as refractory for blast furnace hearths since 1951 in Nippon Steel. Besides excellent corrosion resistance, high thermal conductivity is required for the refractory for blast furnace hearths to help a protective layer form on the hot face by cooling. Nippon Steel has investigated the use of carbon blocks for blown-off blast furnaces, and based on the findings obtained, taken measures to suppress the infiltration of hot metal and improve the corrosion resistance and thermal conductivity of carbon blocks. The corrosion resistance of carbon blocks has been further improved lately by making a protective adhesion layer form at the iron/carbon interface on the hot face.*

## 1. Introduction

The corrosion resistance of carbon blocks for blast furnace hearths has been improved based on the understanding that the principal factors of their wear are (1) the penetration of molten iron into pores, (2) embrittlement of the material on the hot side (loss of cooling capacity), and (3) erosion due to direct contact with molten iron (dissolution by carburizing).<sup>1-4)</sup> In order to prevent the penetration of molten iron, the size of pores was reduced by making the material more dense using Si-O-N whiskers grown in the pores of carbon blocks.<sup>5)</sup> In addition, to prevent erosion due to carburizing dissolution, alumina, which has high strength at high temperatures and is highly resistant to mechanical wear, was added to reduce the area of carbon components exposed at the surface.<sup>6)</sup>

Besides improvement in corrosion resistance through these measures, the thermal conductivity of carbon blocks has also been improved to enhance their cooling capacity to better protect the hearths.<sup>7)</sup> Field tests on the latest micro-pore type carbon blocks after use demonstrated that the occurrence of the embrittled structure that was often seen with older types decreased drastically, significantly contributing to extension of blast furnace campaign life. This also attests to the appropriateness of our basic direction and policy concerning the development of carbon blocks.

## 2. Previous Development of Carbon Blocks

The development of different types of carbon blocks aimed at enhanced corrosion resistance and thermal conductivity is described below (see Fig. 1).

### 2.1 History of development of different types of carbon blocks

In 1965, BC-5 was developed by combining roasted anthracite,

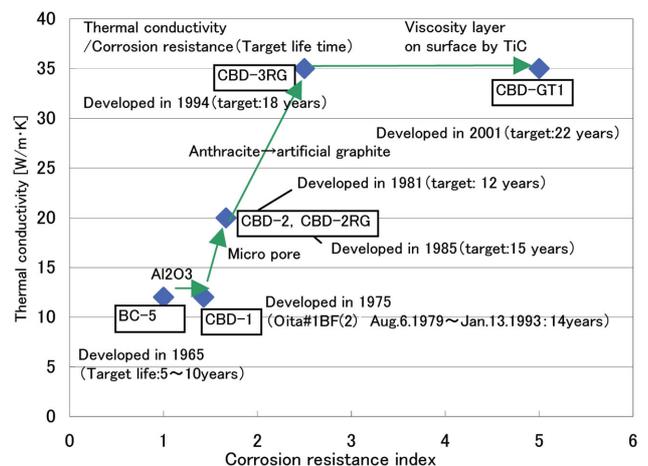


Fig. 1 Development of carbon block

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Table 1 Typical properties of developed carbon block

Carbon block		BC-5	CBD-1	CBD-2	CBD-2RG	CBD-3RG	CBD-GT1
Year of developed		1965	1975	1981	1985	1994	2001
Properties	Bulk density	1.56	1.58	1.59	1.71	1.76	1.96
	Porosity (%)	18.7	17.3	18.5	19.0	23.1	19.7
Compression strength (MPa)		40.5	43.0	45.1	66.9	63.0	76.2
Bending strength (MPa)		11.7	11.9	12.3	15.0	15.2	21.4
Thermal conductivity (W/m • K)		17.1	13.2	13.8	23.3	33.3	37.0
Porosity more than 1 μm (%)		16	11	2.7	1	0.2	0.15
Corrosion resistance (index)		100	140	140	170	250	500

which affords excellent resistance to corrosion by molten pig iron, with artificial graphite, which has high heat conductivity, using tar as the binder for easy extrusion molding. This initial type of carbon block was widely used for a long period. CBD-1 then appeared in 1975, with alumina, which is resistant to acidic slag, added to improve resistance to erosion by molten iron. CBD-2, which was developed in 1981, contained metallic Si so that Si-O-N whiskers would form in pores during the manufacture (firing) to reduce their diameters. Its properties and performance after use were examined at a relining of Muroran No. 2 Blast Furnace.

In the course of development of CBD-2RG, which was commercially used from 1985, the forming method was changed from extrusion molding to press forming, and the binder from tar to resin to increase the material density.<sup>1)</sup> Its properties and condition after use were tested on the occasion of the relining of the No. 4 Blast Furnace at Kimitsu Works. After that, CBD-3RG was developed in 1994 replacing calcined anthracite with fine artificial graphite and alumina to improve thermal conductivity and resistance to molten iron.<sup>2)</sup> Details of CBD-3RG are reported in Section 4.

2.2 CBD-GT1—carbon block with high corrosion resistance

CBD-GT1 was developed to improve corrosion resistance; its high corrosion resistance is due mainly to the intentional forming of a protective layer at the hot face in direct contact with molten metal. Titanium, which is effective in increasing the viscosity of hot metal, was added to the material to increase the viscosity of the protective layer forming at the iron/carbon interface (explained in more detail in Section 5). Table 1 compares the properties of different types of carbon blocks.

3. Field test of Carbon Blocks

CBD-2 was developed with the aim of decreasing the pore size. The authors had a chance to investigate CBD-2 after its use, and evaluated its condition and properties in comparison with those of the conventionally used BC-5.

3.1 Field test of BC-5

Fig. 2 shows the appearance of BC-5 samples taken from the

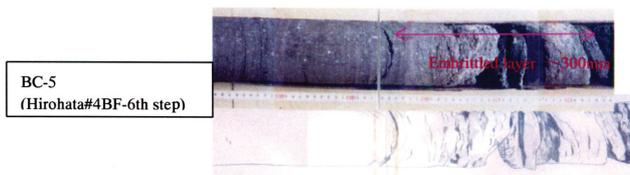


Fig. 2 Core boring specimen of most conventional carbon block after use  
Embrittled layer observed up to 300 mm from hot face

hearth of the No. 4 BF at Hirohata Works by core boring. An embrittled structure was observed to a depth of about 300 mm from the hot face. No infiltration of pig iron was observed, and the material was found to have powdered on the hot-face side. This is presumably because the matrix was destroyed into microscopic fragments because of infiltration into the pores of alien substances (zinc oxide, alkaline compounds, etc.) having different expansion coefficients over a long period.

3.2 Field test of CBD-2

On the occasion of the second relining of Muroran No. 2 BF, samples of CBD-2 were taken by core boring for investigation from three positions at the fifth and seventh levels of the hearth bricks as illustrated in Fig. 3. The following descriptions relate mainly to the sample taken from the seventh level.

1) Visual observation

The thickness of the embrittled layer of CBD-2 (see Fig. 4) was smaller compared with past cases of BC-5 (shown in Fig. 2); whereas the embrittled layer from the Hirohata No. 4 BF was about 300 mm thick, that of CBD-2 from the Muroran No. 2 BF was only about 100 mm.

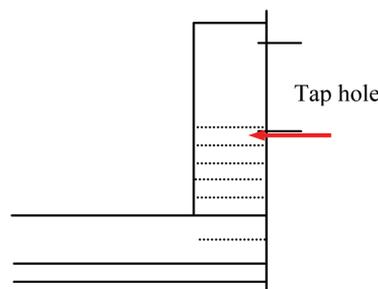


Fig. 3 Core-boring spots

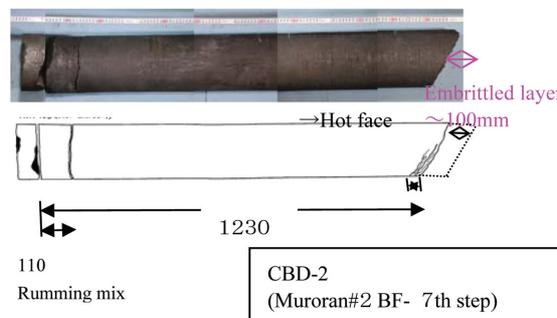


Fig. 4 Schematic view of core-boring specimen

2) Chemical analysis

Fig. 5 shows the distribution of alkaline compounds in the BC-5 and CBD-2 samples. With the CBD-2 sample, the pores of which were finer than those of BC-5, the penetration of alkaline compounds from the hot face was effectively suppressed.

Fig. 6 shows the distribution of ferrous and SiC components in the CBD-2 samples. Whereas iron was found to have penetrated significantly and the amount of SiC was small near the hot face, iron decreased and SiC increased at positions away from the hot face,

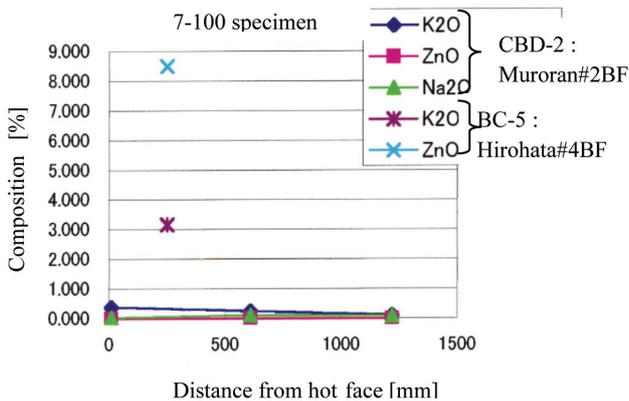


Fig. 5 Alkaline compositions of used CBD-2/BC-5

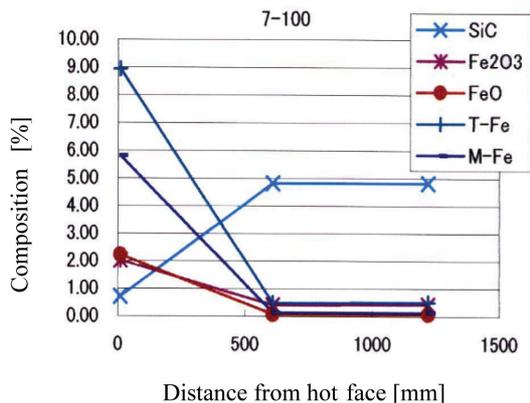


Fig. 6 Iron and SiC compositions of used CBD-2

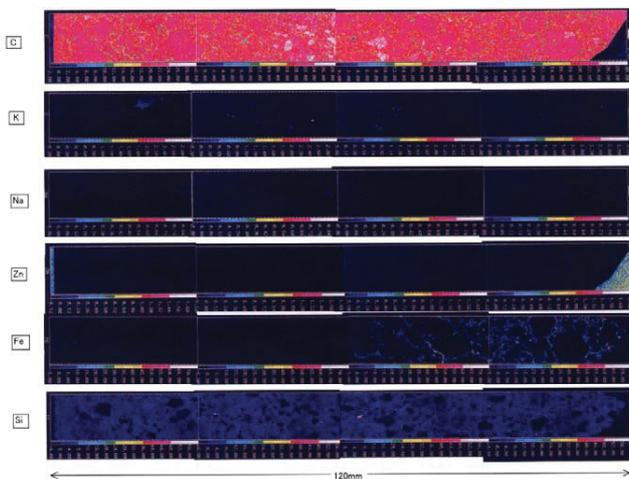


Fig. 7 EPMA maps up to 120 mm from hot face (used CBD-2)

which was the effect of Si addition to make pores finer to suppress the penetration of iron. Fig. 7 shows EPMA maps of the samples; the iron penetration was observed up to a depth of about 60 mm from the hot face.

3.3 Field test of CBD-2RG

On the occasion of the third relining of the Kimitsu No. 4 BF, samples of CBD-2RG were taken by core boring for investigation from four positions, two each at the ninth and tenth levels of the ring carbon. The following descriptions relate mainly to one of the samples taken from the ninth level (see Fig. 8).

1) Visual observation

Whereas the embrittled structure in the samples from the Muroran No. 2 BF was about 100 mm thick, no such structure was seen with the samples of CBD-2RG, and a sound structure was observed across substantially all the sample thickness to the hot face, except for some cracks that presumably formed during the boring.

2) Chemical analysis

Fig. 9 shows the distribution of alkaline compounds in the CBD-2RG samples across the thickness from the hot face to the back; the amounts of infiltrating alkaline compounds were smaller than those in the CBD-2 samples. Fig. 10 shows the distribution of ferrous and SiC compounds. The infiltration of iron was, like that of alkali, far smaller than in CBD-2.

Fig. 11 shows EPMA elementary maps of the CBD-2RG samples up to a depth of 100 mm from the hot face. The maps confirmed the chemical analysis results to the effect that penetration of alien substances was reduced.

3.4 Discussion and Conclusion

The examination of CBD-2 and CBD-2RG after use, which have pores of reduced diameters to make the structure more compact, con-

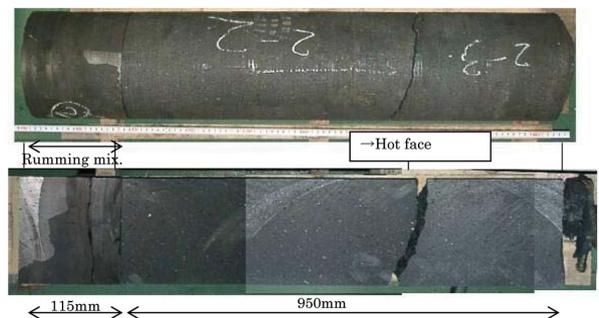


Fig. 8 Appearance of core-boring specimen (CBD-2RG)

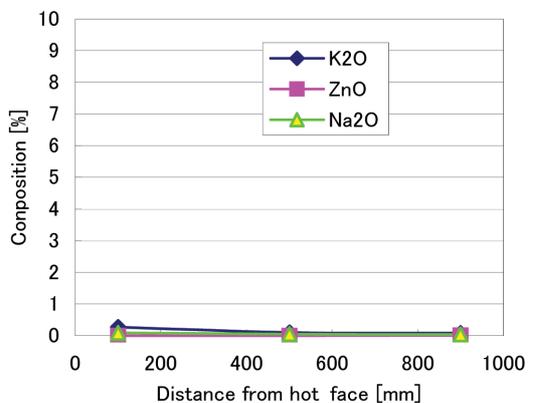


Fig. 9 Alkaline compositions of used CBD-2RG

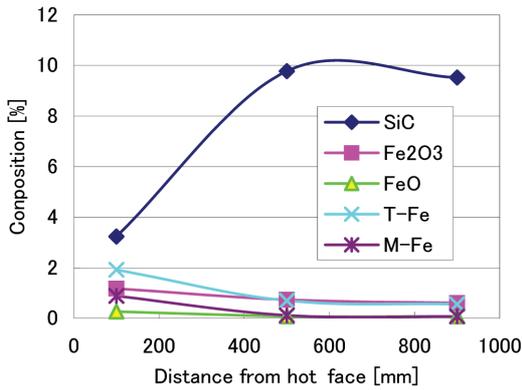


Fig. 10 Iron and SiC compositions of used CBD-2RG

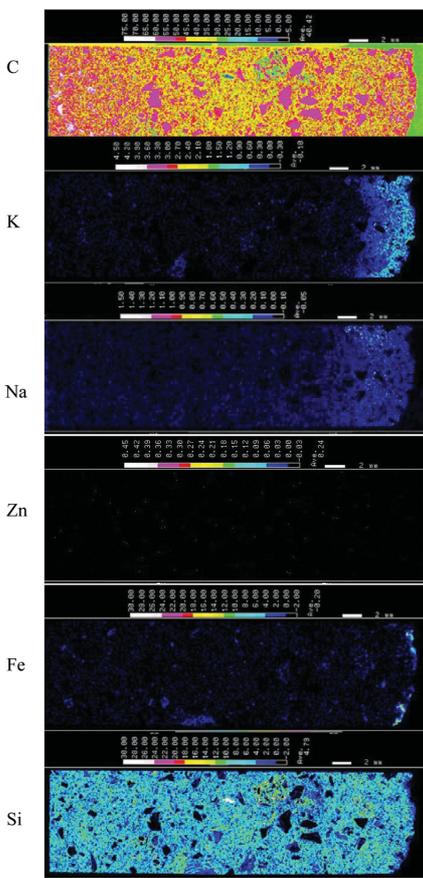


Fig. 11 EPMA maps up to 100 mm from hot face (used CBD-2RG)

firmed that the reduction in pore diameter effectively achieved the development objective to prevent the infiltration of alien substances and the formation of an embrittled structure, which supported the development direction and policy up to CBD-2RG.

#### 4. Development of CBD-3RG—Carbon Block with High Thermal Conductivity<sup>7)</sup>

Conventional types of carbon block were composed of anthracite as the main material with the addition of natural and artificial graphite. Chemical analysis of these carbonaceous materials revealed that anthracite and natural graphite contained ash contents of alu-

mina and silica of 3 to 10 wt %, and that anthracite, especially, contained these ash contents evenly distributed in the structure and had excellent resistance to hot metal (see Fig. 12). Based on this finding, the authors added fine powdered alumina and metallic silicon to artificial graphite, mixed them with a resin binder, and formed the mixture into blocks by press forming (see Fig. 13).

The carbon block thus obtained, which was named CBD-3RG, exhibited a remarkably improved thermal conductivity, and at the same time, corrosion resistance 50% higher than that of CBD-2RG. Table 2 shows the properties of the developed high-thermal-conductivity carbon block, CBD-3RG.

#### 5. Development of CBD-GT1—Carbon Block with High Corrosion Resistance

It was considered impossible to further improve the corrosion resistance of carbon block beyond the level of CBD-3RG using conventional measures to make the material more compact, and hence, the authors envisaged enhancing its corrosion resistance further by use of an additive that would cause self-modification of the material at the hot face.

##### 1) Selection of additive

Conventionally, as common practice at the final stage of a blast furnace campaign, iron sand containing TiO<sub>2</sub> was blown into the furnace through tuyeres to increase the viscosity of hot metal to prevent wear of hearth wall refractory.<sup>8)</sup> When a blast furnace is dismantled for relining after blow-off, deposits of TiN, commonly called “titanium bears”, are sometimes found in the hearth. In consideration of these facts, the authors thought that selecting and adding, at the time of manufacture of carbon blocks, an element capable of increasing the viscosity of molten pig iron such as Ti would be effective in further retarding the erosion of carbon block by hot metal. Fig. 14 shows the effects of different elements to increase the viscosity of hot metal.

In consideration of possible volume change (occurrence of fine cracks) of carbon blocks due to reaction of the added element, it was considered appropriate to add it in carbide form. The authors pre-

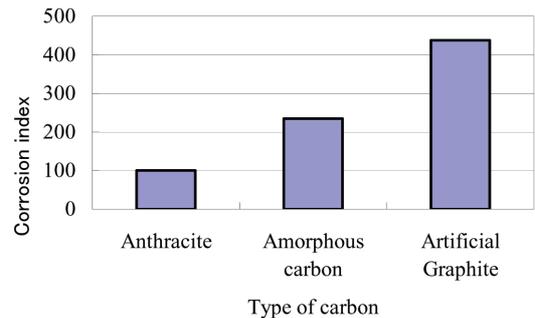


Fig. 12 Corrosion of carbonaceous materials by pig iron at 1 550 for 1 hour

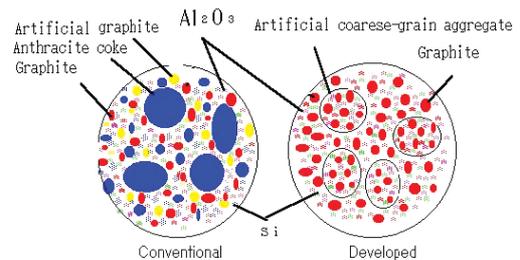


Fig. 13 Schematic representation of formation of carbon materials

Table 2 Properties of carbon block

Composition (wt%)	Conventional carbon block	High thermal conductivity carbon block
	CBD-2RG	CBD-3RG
- Al <sub>2</sub> O <sub>3</sub>	6	9
Si	10	10
Anthracite	44	-
Amorphous carbon	10	-
Artificial graphite	30	81
Thermal conductivity (W/m • K)	23.3	33.3
Corrosion resistance (index)	100	150

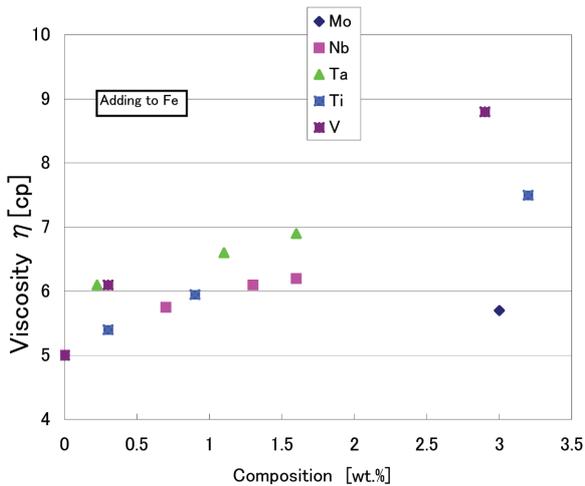


Fig. 14 Fe viscosity at 1550 °C with addition of various elements

Table 3 Corrosion resistance of carbon block with addition of various carbide elements 10wt% (in index with CBD-3RG as 100)

Element	MoC	NbC	TaC	TiC	VC
Corrosion resistance (index)	91	133	125	167	91

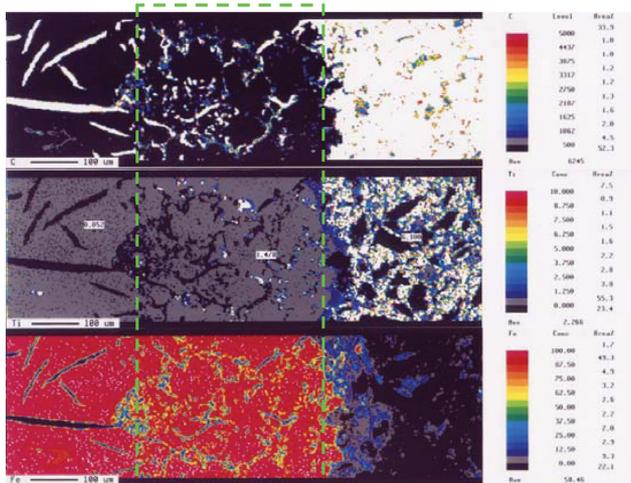


Fig. 15 EPMA mappings at interface between iron and carbon block (upper: C, center: Ti, lower: Fe)

pared carbon block specimens containing carbides of different elements, each by 10 wt %, and evaluated them in terms of their resistance to erosion by molten pig iron. As shown in Table 3, TiC proved to be most effective in improving corrosion resistance. Thus, TiC was selected as the additive.

2) Presumed mechanism of corrosion resistance improvement

The authors tested the carbon blocks with added TiC in terms of their resistance to erosion by molten pig iron. Fig. 15 shows EPMA maps taken at an iron/carbon interface section of a specimen after the test. At the surface of the carbon block contacting hot metal, there is a layer, 100 to 200 μm thick (the area surrounded by the dotted line in green), containing a higher amount of Ti than the rest. In this layer, which is presumably composed of substances that eluted from the carbon block, the viscosity of hot metal is higher than in regions further from the carbon block, and thus the layer is considered to act as a passivated zone serving to protect against corrosion of the carbon block.

6. Closing

Carbon blocks have been used for blast furnace hearths to extend their campaign life. Various types of carbon blocks have been developed through measures such as:

- 1) Addition of fine alumina, highly resistant to hot metal;
- 2) Reduction of pore diameters to prevent penetration of alien matter and hot metal;
- 3) Increase in thermal conductivity to lower the hot-face temperature to improve corrosion resistance; and
- 4) Addition of TiC to increase the viscosity of molten pig iron at the iron/carbon interface to retard the hot metal flow to prevent erosion and thus improve corrosion resistance.

The effects of 1) and 2) above have been confirmed through field tests during blast furnace relining campaigns, which corroborates the appropriateness of past direction and policy of our development.

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