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Investigation of Used Carbon Blocks for Blast Furnace Hearth and Development of Carbon Blocks with High Thermal Conductivity and High Corrosion Resistance

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Abstract

As refractories for the blast furnace hearth, carbon blocks were used in this half century. Blast furnace hearth requires corrosion resistance and thermal conductivity for control self-protection layer. Nippon Steel had developed carbon blocks since 1965.

1. Introduction

Nippon Steel has continually developed new carbon blocks for blast furnace hearths that have higher corrosion resistance. The company considers that the causes of wear of the carbon blocks used for blast furnace hearths are:

1) Penetration of molten iron into pores in the carbon blocks
2) Formation of a brittle layer on the hot face (loss of cooling ability)
3) Fusion damage to carbon blocks caused by direct contact with molten iron (melting through carbonization).

To prevent penetration of molten iron, pores in the carbon blocks have been reduced in size (micro-pores). Micro-pores have been achieved by reducing the pore diameter with whiskers of Si-O-N that grow within the pores in each carbon block. In addition, to reduce the carbon component surface area exposed to molten iron, alumina having excellent high temperature strength and good resistance to mechanical wear is added to the carbon blocks. Thus, carbon blocks that are free of fusion damage due to melting through carbonization have been developed[1].

Furthermore, carbon blocks having better corrosion resistance and high thermal conductivity to allow for reinforcement of the hearth protection have been developed[2]. In a recent examination of used carbon blocks with micro-pores, it was confirmed that the brittle layer that had been formed on them was much less conspicuous than that formed on conventional carbon blocks and that carbon blocks with micro-pores had helped prolong the blast furnace life. Thus, our policy concerning the development of carbon blocks has been validated.

2. History of Development of Carbon Blocks for Blast Furnace Hearth

The carbon blocks that the company has developed with the emphasis on better corrosion resistance and higher thermal conductivity are introduced below (**Fig. 1**).

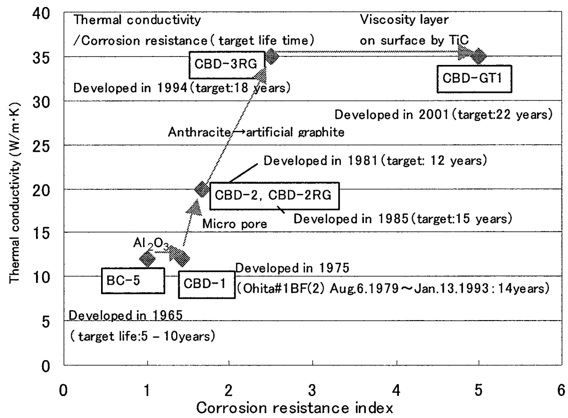

Fig. 1 Development of carbon block

2.1 Development of carbon blocks

BC-5 is a type of carbon block which has long been widely used. Combining the good molten iron resistance of calcined anthracite and the high thermal conductivity of artificial graphite, BC-5 was developed in 1965 using extrusion-moldable tar as the binder. CBD-1 was developed in 1975 with the aim of obtaining better wear resistance to molten iron. To ensure good corrosion resistance, alumina with excellent resistance to acid slag was added. CBD-2, developed in 1981, is a carbon block with metallic Si added and provided with micro-pores produced by forming Si-O-N whiskers in the pores during the baking process. This carbon block was subjected to an in-depth analysis when the No. 2 BF of Nippon Steel Muroran Works was relined. CBD-2RG, developed in 1985, is an improved version of BC-5 that is press-formed (as opposed to extrusion-formed) and that uses a resin binder (in place of the tar binder) to obtain a more dense carbon block[1].

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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
Developed in (year)		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 μ m (%)		16	11	2.7	1	0.2	0.15
Corrosion resistance (Index)		100	140	140	170	250	500

CBD-3RG was developed in 1994 with attention paid to calcined anthracite, which is originally contained in carbon block and which offers excellent resistance to molten iron. The advantageous characteristic of calcined anthracite was achieved through the combination of artificial graphite and alumina powder to develop a carbon block with high thermal conductivity[2]. This carbon block is described in Section 4.

2.2 New carbon block CBD-GT1 with excellent corrosion resistance

CBD-GT1 is a carbon block offering excellent corrosion resistance that is based on the new concept of positively forming a protective layer on the carbon block surface that comes into direct contact with the molten iron. In order to form a highly viscous layer on its surface, the carbon block is dosed with Ti that is used to increase the viscosity of molten iron (see Section 5).

The principal properties of the carbon blocks described above are shown in **Table 1**.

3. Examination of Used Carbon Blocks

As mentioned earlier, the authors had an opportunity to make an in-depth analysis of CBD-2 that had been developed with the aim of achieving micro-pores. They evaluated (as a confirmation of effects) CBD-2 in comparison to BC-5, which has long been used for blast furnace hearths.

3.1 BC-5

Fig. 2 shows the appearance of a core-bored sample of carbon block BC-5 taken from the basin of the No. 4 blast furnace of Nippon Steel Hirohata Works. A brittle layer about 300 mm in thickness can be seen. There are no signs of molten iron penetration, and the hot-face side of the carbon block has partly disintegrated. This is considered to be due to micro-destruction of the carbon block matrix over a long period of time by the external components of varying expansion coefficients that had entered the pores in the carbon block.

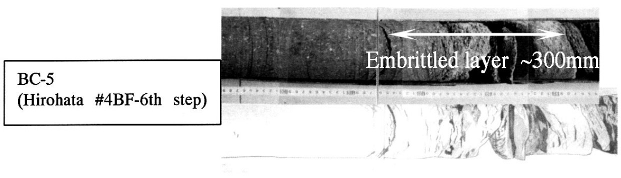

Fig. 2 Core boring specimen of most conventional carbon block after use: Embrittled layer observed about 300mm area in hot-face (right)

3.2 CBD-2

During the second relining of the No. 2 blast furnace at Nippon Steel's Muroran Works, an analysis of core-bored samples of CBD-2 was possible. The sampling points were stages 5 and 7 of the hearth basin (see **Fig. 3**). A total of three carbon blocks were subjected to core boring. The following discussion focuses on the core-bored samples collected from stage 7.

1) Appearance of sample

It was confirmed that as compared with the appearance of the core-bored sample of carbon block BC-5 developed earlier (Fig. 2), the thickness of the brittle layer on the core-bored sample of CBD-2 (**Fig. 4**) was much smaller. The brittle layer on the sample collected from the No. 2 blast furnace of Hokkai Steel Muroran Works was about 100 mm thick, whereas the brittle layer on BC-5 used for the No. 4 blast furnace of Hirohata Works was about 300 mm.

2) Analytical study

Fig. 5 shows the alkaline component distribution in samples of

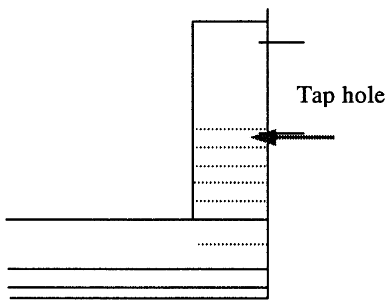

Fig. 3 Core-boring spots

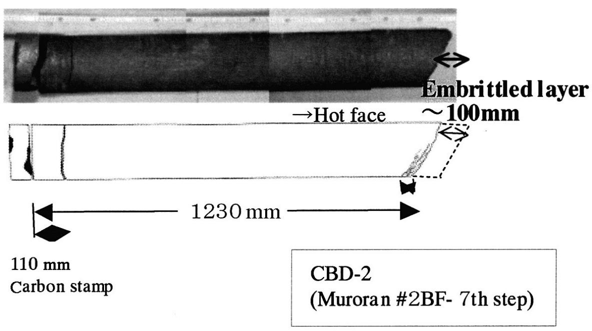

Fig. 4 Schematic view of core-boring specimen

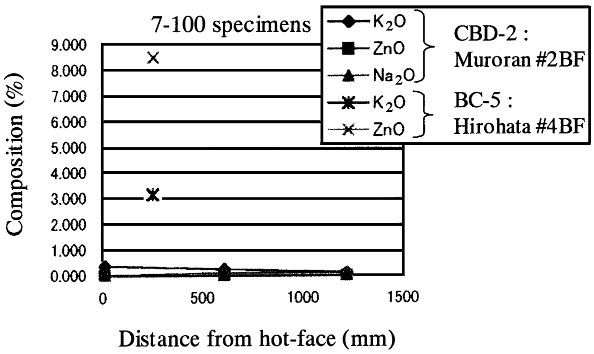

Fig. 5 Alkaline composition of CBD-2 and BC-5

CBD-2 and BC-5, respectively. It was confirmed that compared with BC-5, the CBD-2 with micro-pores had admirably restrained the penetration of alkaline components and that the degree of penetration of alkaline components from the hot face was very small.

Fig. 6 shows the iron and SiC component distributions in samples of CBD-2. The proportion of SiC at the hot face is small due to the penetration of ferrous components. However, with the increase in

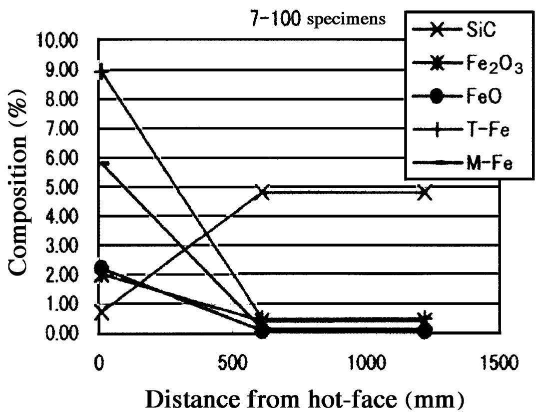

Fig. 6 Iron and SiC composition of used CBD-2

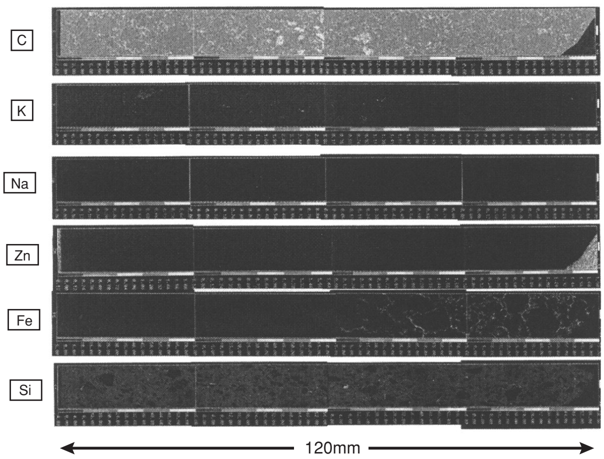

Fig. 7 EPMA-map on the hot-face side 120mm area

distance from the hot face, the proportion of SiC increases and the proportions of ferrous components decrease, indicating that the penetration of ferrous components were restrained by the addition of Si to achieve micro-pores. **Fig. 7** shows an EPMA map of the CBD-2 sample portion up to 120 mm from the hot face. Ferrous components had penetrated up to about 60 mm from the hot face.

3) Analysis results

The results of our analysis of used CBD-2 carbon blocks with micro-pores showed that the original aims for the development of CBD-2 – restraining the penetration of external components and the formation of a brittle layer – had been achieved. Thus, the company's policy on development of carbon blocks was validated.

4. Development of Carbon Block CBD-3RG with High Thermal Conductivity[2)]

The conventional carbon block (CBD-2RG) was made mainly of anthracite (the principal raw material), amorphous carbon and artificial graphite. Following analysis of those raw material carbons, it was found that anthracite and amorphous carbon contained 3 to 10 wt% of alumina and silica as their ash components and that anthracite, in which alumina and silica are evenly distributed, had excellent resistance to molten iron (see **Fig. 8**). On the basis of the analysis results, the company manufactured a new carbon block (CBD-3RG) by press-forming a mixture of artificial graphite, to which alumina powder and metallic silicon were added, and resin binder (see **Fig. 9**).

CBD-3RG proved to have exceptionally high thermal conductivity, as well as excellent corrosion resistance – 50% higher than that of CBD-2RG. The principal properties of the new carbon block CBD-3RG are shown in **Table 2**.

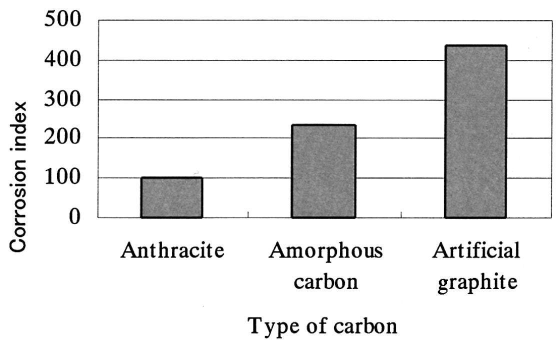

Fig. 8 Corrosion of carbon to pig-iron at 1550℃ for 1 hour

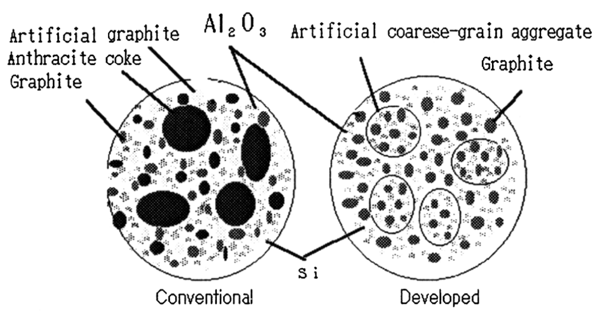

Fig. 9 Schematic representation of formation of carbon materials

Table 2 Properties of carbon block

Composition (wt.%)	Conventional carbon block CBD-2RG	High thermal conductivity carbon block CBD-3RG
α-Al_2O_3	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

5. Development of Carbon Block CBD-GT1 with Excellent Corrosion Resistance

The corrosion resistance of the conventional carbon blocks could no longer be improved simply by making them denser and thereby increasing their wear resistance. Therefore, the company attempted to improve the corrosion resistance of carbon blocks by adding a material which helps form a self-protective layer on their surface.

1) Study of material to be added

The company had learned from experience that injecting TiO_2 in the form of iron sand into a superannuated blast furnace through the tuyere helps restrain the wear of the furnace refractory material since it makes the molten iron more viscous[3]. In addition, the company had noticed a deposit of TiN called Ti bear on the bottom of the furnace. Therefore, in order to further improve the molten iron resistance of carbon blocks, it was considered effective to previously add Ti, or some other suitable element that helps increase the viscosity (lower the fluidity) of molten iron, to the carbon block. The elements that have this effect are shown in **Fig. 10**.

It was decided to add a suitable element in the form of carbide so that it would not cause a change in volume of the carbon block (occurrence of micro-cracks) through chemical reaction. The results of evaluation of corrosion resistance of carbon blocks added with 10 wt% of one of the various types of carbide are shown in **Table 3**. Since TiC was found to be the most effective in improving the corrosion resistance, it was adopted as the material to be added to the carbon block.

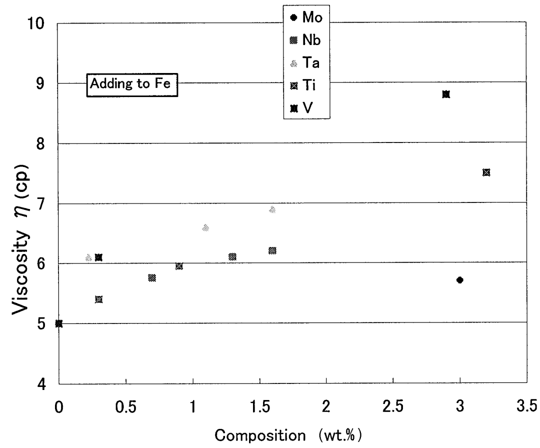

Fig. 10 Fe viscosity at 1550℃ by adding various element

Table 3 Corrosion resistance of carbon block with various carbide element (10wt.% added, index of CBD-3RG: 100)

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

2) Assumed mechanism of improvement in corrosion resistance

Fig. 11 shows the results of EPMA of the interface between molten iron and carbon block with TiC added after a test to evaluate corrosion resistance. A layer containing a relatively large amount of Ti (100 to 200 μ m) is found on the carbon block surface in the interface with the molten iron (the part enclosed in dotted lines in Fig. 11). Apparently, this layer was formed by Ti that had melted out from the

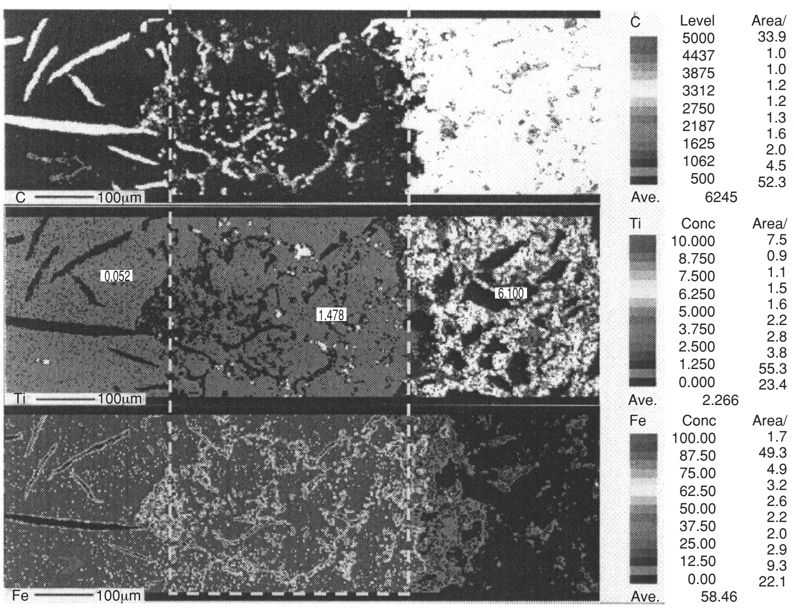

Fig. 11 EPMA of surface area iron/carbon block

carbon block. It is estimated that as the viscosity of the carbon block relative to the molten iron increased, the Ti contained in the carbon block became passive and formed a protective layer that improved the corrosion resistance of the carbon block.

6. Conclusion

With the aim of extending blast furnace life, the company has continually developed new carbon blocks for blast furnace hearth as follows.

1) Addition of alumina powder offering good resistance to molten iron
2) Achievement of micro-pores to prevent penetration of external components and molten iron into the carbon blocks
3) Improvement in thermal conductivity of carbon blocks to lower their surface temperature and corrosion resistance
4) Addition of TiC, which increases the viscosity of molten iron at the interface with the carbon block, prevents fusion damage to the carbon block by a stagnating molten iron flow, and improves corrosion resistance of carbon block.

The results of an analysis of used carbon blocks with micro-pores have validated the company's policy on development of carbon blocks.

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