

Carbon Blocks for Blast Furnace Hearth Refractories

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Abstract

Carbon blocks for blast furnace hearth refractories have been used by Nippon Steel Corporation for the past half century. As refractories of blast furnace hearths, carbon blocks are required to have corrosion resistance and thermal conductivity so that the self-protection layer on their hot surface can be controlled. Nippon Steel investigated the blast furnace hearth refractories, and analyzed and improved the carbon blocks applied to blast furnace hearths.

1. Introduction

A blast furnace is a reduction furnace that produces molten iron from iron ore, for which hearth refractory, a material that holds the carbon-saturated molten iron produced and contributes to a long campaign and the stabilization of the furnace structure, is required. Carbon blocks are made of mainly carbonaceous material and are difficult to dissolve into carbon-saturated molten iron (carburizing dissolution). Carbon blocks have relatively high thermal conductivity compared with those of other refractories of oxidized metal systems, and they efficiently protect the hot face. Carbon blocks were first applied in Europe and the US in the early twentieth century and have been used ever since. As the employment of high top-pressure blast furnace operation for higher production requires the development of more durable refractories and for more stabilized operation, carbon blocks for exclusive use for blast furnace hearths have been improved. Enhanced durability carbon block has been promoted by clarifying the corrosion mechanism based on the precise investigation and analysis of used carbon block.

Nippon Steel Corporation considered the following factors as the causes of the damage and erosion of the carbon blocks of blast furnace hearths and promoted the improvement of corrosion resistance.¹⁻⁴⁾

- 1) Penetration of molten iron into carbon block pores.
- 2) Formation of embrittled structure below the hot face (loss of cooling capability)
- 3) Erosion of carbon block due to direct contact with molten iron (carburizing dissolution)

To prevent molten iron penetration, the pores were micronized for densification.⁵⁾ As a method of densification, the pores were micronized by Si-O-N whiskers that grow in the pores of carbon blocks. In a developed carbon block,⁶⁾ to prevent the erosion due to carburizing dissolution, alumina having high strength at high tem-

peratures and excellent in resistance to mechanical erosion was added to reduce the area of contact of the carbon composition with the molten iron on the carbon block surface. Additionally, carbon blocks having high thermal conductivity targeted at the intensification of the protection of the furnace hearth by enhancing the cooling capability as well as corrosion resistance have been developed.⁷⁾ Based on the investigation conducted on a blast furnace after its termination of a campaign, in the carbon blocks wherein pores were micronized, a significant decrease in embrittled structure that existed in conventional carbon blocks was recognized and the contribution of pore micronization to the extension of a blast furnace life campaign was confirmed. Furthermore, with the use of the carbon blocks in which the pores were micronized and maintained and the thermal conductivity was enhanced, a significant decrease in the erosion rate during operation and the elimination of the embrittled layer were confirmed. A great improvement in the furnace hearth refractory erosion has thus been realized.

2. Development of Blast Furnace Hearth Carbon Blocks

Carbon blocks targeting the enhancement of corrosion resistance and high thermal conductivity have been developed following the steps of densification (micronization of pores), enhancement of the thermal conductivity and the formation of the hot face protective layer (**Fig. 1, Table 1**). In Fig. 1, the first generation carbon blocks I made of carbonaceous material for the electrode were developed in the early stages and became commercially available in the market. This was followed by the development of carbon blocks II to IV developed in the said order, the outline of which is explained hereunder.

2.1 Development of densification and result of investigation

After "I" (the result of the investigation in 1965 is shown in **Fig.**

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Table 1 Typical properties of developed carbon block

Carbon block		I	II	III	IV	V	VI
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	23.1	19.7
Compression strength [MPa]		40.5	43	45.1	66.9	63	76.2
Bending strength [MPa]		11.7	11.9	12.3	15	15.2	21.4
Thermal conductivity [W/(m·K)]		17.1	13.2	13.8	23.3	33.3	37
Porosity more than 1 μm [%]		16	11	2.7	1	0.2	0.15
Corrosion resistance [index]		100	140	140	170	250	500

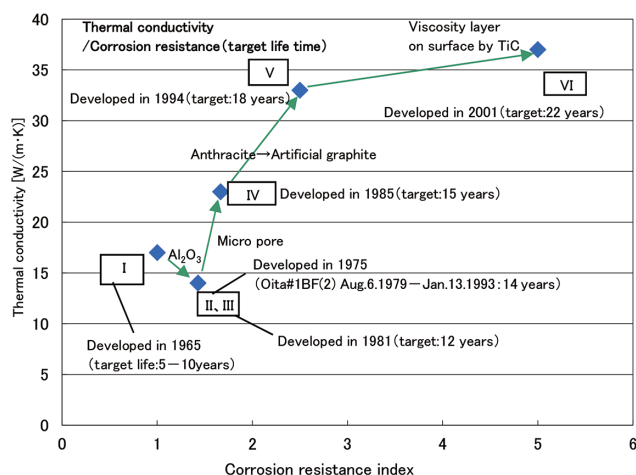


Fig. 1 Development of carbon block

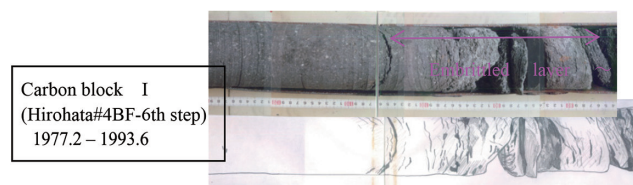


Fig. 2 Core-boring specimen of most conventional carbon block after use (embrittled layer observed about 300 mm area in hot-face (right))

2), “II” was developed in 1975. In “I”, based on the carbon blocks that had been widely used in electric furnaces, the excellent resistance of roasted anthracite to molten iron and the high thermal conductivity of artificial graphite were exploited in combination, using the easy extrusion molding material tar as a binder. “II” was developed in 1975, in which alumina having a high wear resistance to acidic blast furnace slag was added to enhance the wear resistance to molten iron. By adding metallic Si and by forming Si-O-N whiskers in pores in burning, “III” with micronized pores was developed in 1981 (due to the development of analysis technology that followed, mainly through the observation by electron microscope FE-SEM, the existence of C nanofibers and SiC nanostructures was confirmed⁸⁾). The result of III was investigated and analyzed during the secondary relining work of the Murooran No.2 Blast Furnace (Figs. 3, 4) and it was confirmed that, although complete elimination of embrittled structure was not achieved, the preventive effect against the penetration of alien compositions was confirmed (Fig. 5 shows the penetration of Fe composition to a depth of 60 mm).

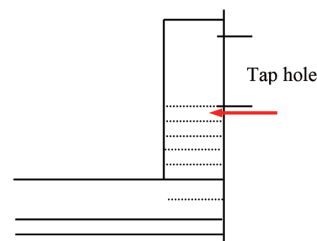


Fig. 3 Core-boring spots

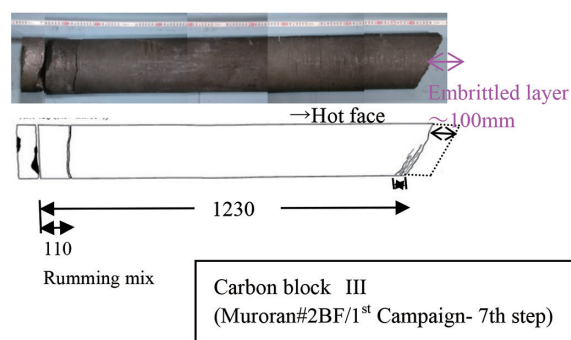


Fig. 4 Schematic view of core-boring specimen (III)

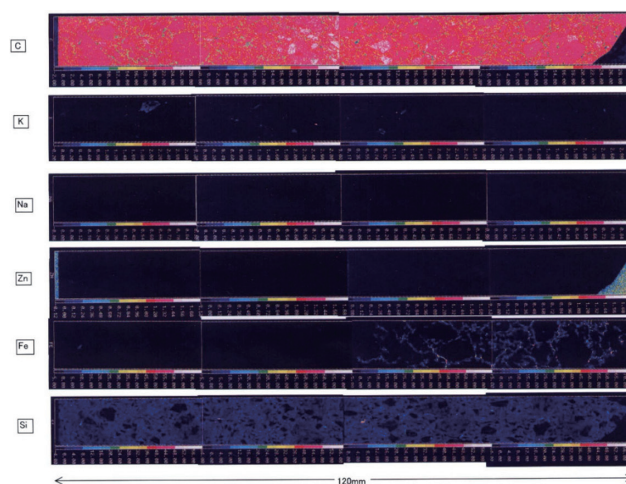


Fig. 5 EPMA-map on the hot-face side 120 mm area (III)

Next, “IV” was developed in 1985, in which, to promote further densification, the molding method was changed from extrusion molding to press forming, and at the same time, the binder was changed from tar to resin. As a result of the investigation and analy-

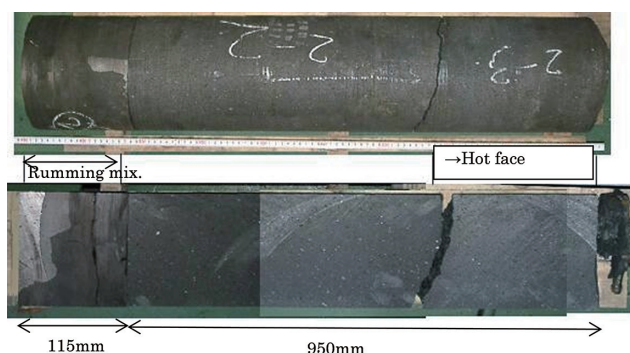


Fig. 6 Schematic view of core-boring specimen (IV)

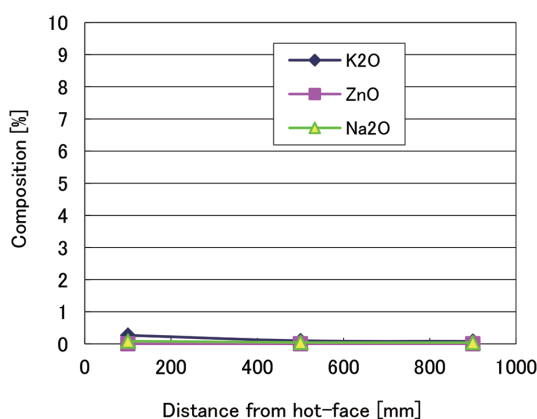


Fig. 7 Alkaline compositions of used IV

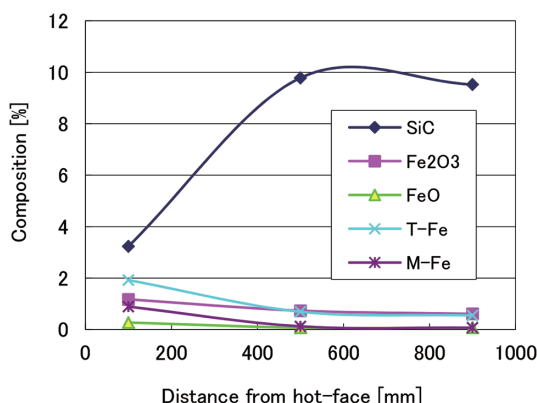


Fig. 8 Iron and SiC compositions of used IV

sis conducted in the third relining work of the Kimitsu No.4 Blast Furnace (Figs. 6, 7 and 8), it was confirmed that the function of preventing the penetration of alien compositions was effectively working except the penetration of alkaline compositions of Na and K to a depth of about 5 mm from the hot face (Fig. 9).

2.2 Development of high conductivity material and result of investigation

Roasted anthracite excellent in resistance to molten iron and existing in the carbon block material was investigated and by creating the same effect through the synthesis of artificial graphite and alumina fine powder, the carbon block “V” having high thermal conductivity was developed in 1994.⁷⁾ As a result of the investigation conducted on the Kimitsu No.3 Blast furnace in operation after its

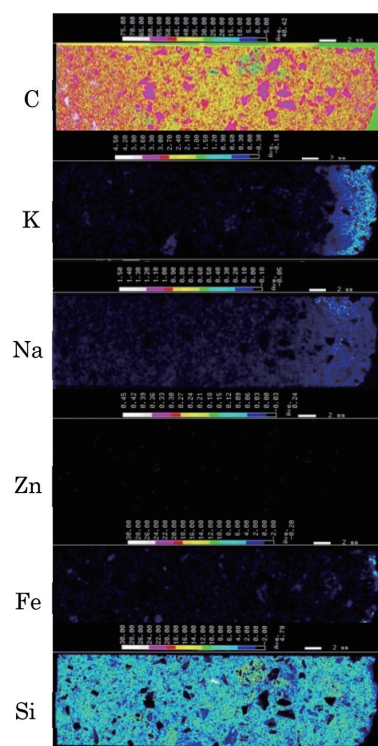


Fig. 9 EPMA-map on the hot-face side 100 mm area (used IV)

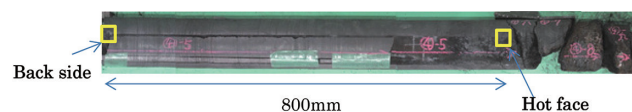


Fig. 10 Core-boring specimen 10th step around #2TH on Kimitsu #3BF(3) campaign (V)

third relining work (Fig. 10), no penetration of alien compositions was indicated (Figs. 11, 12).

In particular, the penetration of alkaline (K, Na) compositions into the hot face observed in the investigation of IV was suppressed in V, and furthermore enhanced life duration due to the improvement of the cooling capacity of the hot face realized by the improvement of the thermal conductivity was confirmed.

2.3 Development of material equipped with surface-protection function

Based on the operation of blowing-in TiO₂-bearing iron sand through tuyers near the termination of a blast furnace campaign to create viscosity in molten iron and to prevent the erosion of the hearth wall refractories⁹⁾, and based on the TiN deposit termed as “titan bear,” being observed as adhering to the furnace hearth, carbon blocks “VI” having a surface protective layer that decreases the molten iron fluidity on the carbon block surface and provides higher resistance to molten iron was developed in 2001.¹⁰⁾

Since Ti added to carbon blocks is carburized to TiC by the heat received during operation, by adding TiC as a part of the material from the very beginning, stable material characteristics have been obtained. From the result of the analysis of the section of the interface surface obtained from a test conducted to evaluate the corrosion resistance of carbon block vs. molten iron (Fig. 13), a Ti composition dissolved to molten iron remains on the surface and forms a viscous protective layer. Whereas the investigation to be conducted

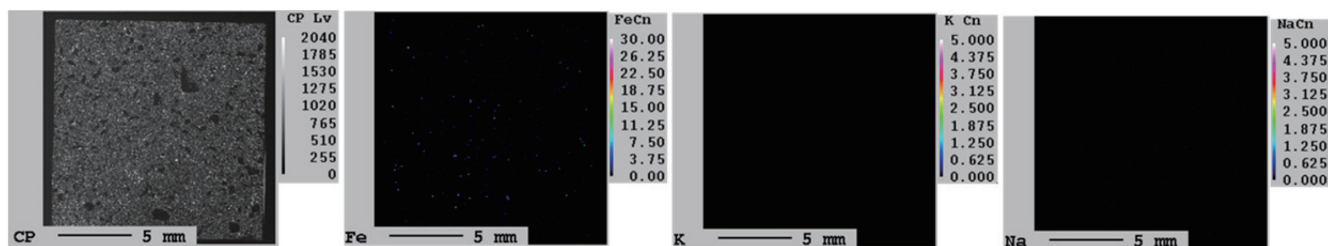


Fig. 11 EPMA analysis on hot-face side (carbon block V)

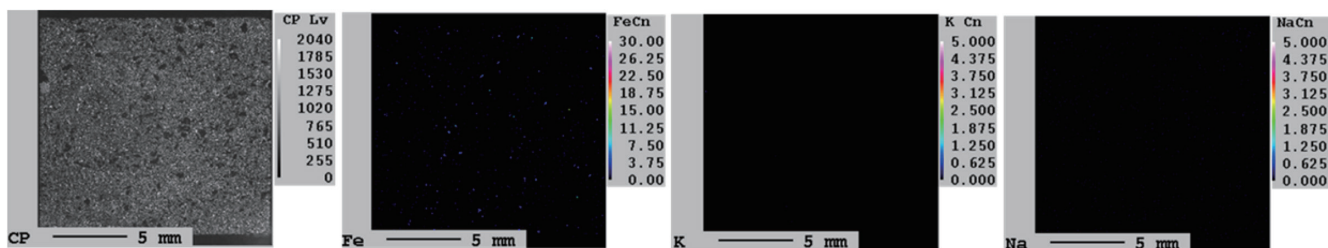


Fig. 12 EPMA analysis on back side (carbon block V)

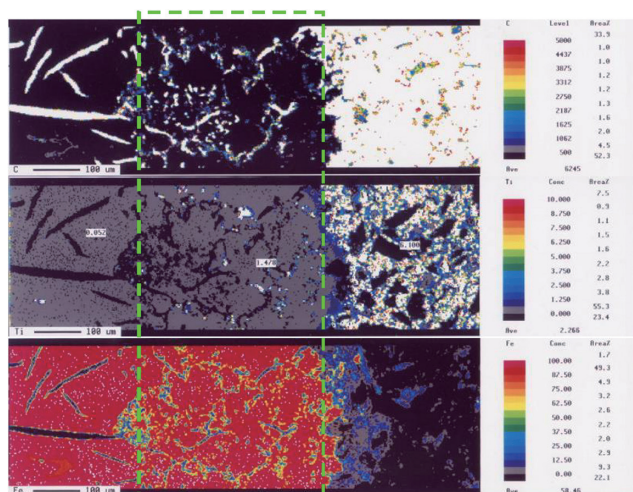


Fig. 13 EPMA analysis on carbon block VI surface (inside the dotted line)

on sampling after the termination of a campaign is not yet available, since, at this moment, the blast furnace that employs these carbon blocks is under operation, by non-destructive estimation (estimation of remaining thickness with temperatures), the effect of extending the furnace life to higher than those of the carbon blocks ever developed has been confirmed (Fig. 14).¹¹⁾

3. Conclusion

Carbon blocks used for furnace hearths targeting longer blast furnace campaign life have been developed through the following process.

- 1) Addition of alumina fine powder having high resistance to molten iron
- 2) Micronization of pores to prevent the penetration of alien compositions and molten iron
- 3) Enhancement of the thermal conductivity to lower the hot face temperature and to improve the corrosion resistance
- 4) Addition of TiC to enhance the viscosity of the molten iron on the interface surface to prevent the erosion by retarding the

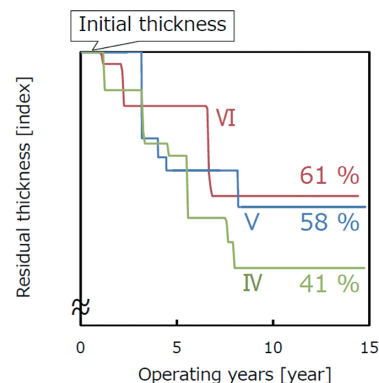


Fig. 14 Trends of residual thickness of carbon block (IV-VI)

molten iron flow and to enhance corrosion resistance

Since a blast furnace has a huge cooling structure, to extend its life span as a reactor vessel, not only from the viewpoint of simply developing materials alone, it is also important to enhance the technological capabilities to support the function of protecting the hot interfacial surface, taking into account the balance of the entire equipment. We are determined to continue the investigation of the used refractories in the blast furnace relining period and to make efforts to pursue higher stabilization of the iron production equipment through further improvements.

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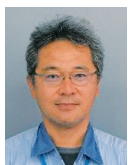
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