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Technological Philosophy and Perspective of Nanotech Refractories

Shinichi TAMURA* Tsunemi OCHIAI
Taijiro MATSUI Kiyoshi GOTO

Abstract

In recent years, in refractories industry, a cost supreme principle occupies the mainstream and even a technical feeling of a blockade is sensed. Much more high purity steel and strict component control steel will be reqired in the future, and the request to the ultra low carbon containing refractories in refining and casting of steel is indispensable. Realization of nanotech refractories based on the nano structural matrix is expected as a leading measure. If the further leap of refractories technology is aimed at, introduction of the new technology which exceeded the existing frame on the occasion of development is indispensable. In this report, with the following two control technologies, nano structural matrix is developed and the direction towards utilization of nanotech. Refractories is shown two control technologies are, a)control of the packing structure by dispersion of the nano particles of various shapes, or the pore structure by modification on the surface of a coarse grains, and b)control of the combined structure in the heat-treatment process of binding materials.

1. Introduction

The refractory industry has long been considered mature. In recent years, the cost-first principle that was triggered by the importation of inexpensive refractory materials from abroad has prevailed, and there is some sense of stagnation in terms of refractory technology.

But thanks to the strong recovery of the global economy in recent years, the steel market has enjoyed a resurgence. In this market, much is expected of Japan's high-grade steels, such as those for automobiles, which require sophisticated manufacturing technology. However, in view of the fact that the Japanese steel industry is shifting its emphasis from quantity to quality, it cannot be said that refractory technology—which has developed in tandem with the steel industry—is in a completely satisfactory condition.

Certainly, many new refractory technologies have been developed as needed to meet the specific needs of the steel industry. However, it seems unlikely that existing refractory technology will be able to fully meet the industry's future needs.

Under present international economic conditions, it is reasonable for Japan to import inexpensive refractory materials from abroad. In order to intensify the originality and competitive edge of the Japanese steel industry, however, it is considered indispensable to develop new refractories suited to the production of higher-grade steels, new brickwork/refractory maintenance techniques that take into account a dwindling labor market amidst a demanding working envi-

* Executive Counselor & Chief Researcher at Japan Technical Information Services Corporation
3-25-23, Takanawa, Minato-ku, Tokyo

ronment, and new types of environment-friendly refractories that help conserve natural resources. In this regard, attention should be paid to the fact that Japan imports the bulk of the raw materials for the refractories it needs from only a few countries.

Since refractories have a long history, R&D into refractories based on conventional technical concepts and techniques seems to have been conducted fairly exhaustively. If further refinement of refractory technology is hoped for, the introduction of revolutionary new technologies is considered indispensable.

Of those new technologies, nanotechnology is considered especially promising. Refractories are made up of small particles with dimensions of several millimeters or less. At present, fine micron-level particles are mainly used for refractories. In this paper, the application of nano particles with dimensions of 100 nm or less is discussed. Nano particles are almost molecular scale, and are the smallest unit to show refractory properties. It is expected that they will be capable of unique activation. In addition, nano particles develop interesting phenomena in terms of packing, pore formation, binding, etc. Nippon Steel has conducted R&D to create characteristic microstructures by controlling the reaction process of organic substances used as binders. At present, the emphasis of this development is on building a nano structural matrix, including nano particles and a microstructure created by the above process.

2. Process of Developing a Nanotech Refractory

2.1 The way to the development of nanotech refractories

With the exception of certain types of fusion-cast refractories, almost all refractories involve an aggregate of small particles. They are made from a formed material which has a very wide particle-size distribution, from several microns (fine particles) to several millimeters (coarse particles) across. Unlike fine ceramics which are made by subjecting a formed material consisting of particles of almost uniform size to an extremely large firing shrinkage for densification to 30 wt% to 50 wt% (because of this large change in volume, it is difficult to manufacture large ceramic products in bulk), refractories which effectively utilize the wide particle-size distribution are free from such large firing shrinkage even when the formed material is subjected to high-temperature firing/hysteresis for the densest packing or pore-shape control. In addition, the structure of a refractory has a greater effect on the properties of the refractory than composition control.[1, 2] It may be said that a refractory that displays super resistance to thermal shock and corrosion when its structure is designed appropriately is hardly an old material compared to fine ceramics, but rather a functional material which can be used in a grueling environment.

The refractory is a composite material made up of a solid and gas. Its properties are determined by the size, amount, shape and distribution of pores and by the packing structure of solid particles and the mode of binding at their points of contact. The principal characteristics of a refractory with a wide particle-size distribution are governed by an aggregate of fine particles which bind coarse and medium-sized particles together. This aggregate, which consists of fine particles of 44 μm/or less (325-mesh undersize), is generally called a matrix. Despite the fact that the pores and pore structure in the matrix significantly influence the resistance of the refractory to thermal shock and penetration/erosion by molten metal, it seems that R&D into new technologies that can be applied to the matrix is lagging.

Ordinarily, in the field of conventional refractories, it is fine particles several micrometers in size that are routinely subjected to blending control. This paper describes the development of a "nano structural matrix"—an original technology whereby a nano region is established in an ordinary matrix. For the purpose of this development, nanotechnology was positively applied.[3)]

The nano structural matrix itself is an unexplored region in the field of refractories. In terms of the nano particles available at the present stage, particles which are tens to hundreds of nanometers in size were considered. Attempts were made to reduce the size of the pores and control the number of pores in the particle-packing process by systematically adding nano particles which are smaller than fine particles to an ordinary matrix and varying the refractory elasticity by controlling the intensity of the binding, etc. at the points of contact between fine particles and nano particles with special characteristics. As a result, it was found that controlling the pore structure and binding characteristic affords the potential to improve both thermal shock resistance (spalling resistance) and corrosion resistance to molten metal at the same time (processes that were formerly considered extremely difficult).

2.2 Development of nanotech refractory

2.2.1 Selection of nano particles

A good example of the successful industrial use of nano particles is found in the automotive tire industry. Carbon black, which is made up of nano particles, is mixed into the rubber material for tires as the filler. Initially, a single-sphere type carbon black with a particle size of about 100 nm was used. This was first replaced by carbon black of an aggregate type having a particle size of 50 nm, and then by carbon black of the same type having a particle size of little more than 10 nm. It has been reported that the use of nano particles (carbon black) has dramatically improved tire wear resistance and thereby increased their longevity (before changing tires is required) by an order of magnitude.[4)]

Based on tires containing carbon black as an example of a composite of nano particles, it was considered that nano particles could also be used in refractories as a composite with similar technical aspects to those of tires. Nano particles which had been dispersed within the texture of a tire were observed under a microscope (**Fig. 1**). These observations convinced us that it should be possible to build a nano structural matrix for a refractory by taking advantage of the functions of single-sphere or aggregate type carbon black, although no small difficulty would be involved in dispersing such nano particles throughout the texture of the refractory. It should be noted, however, that unlike automotive tires, the refractory is exposed to extremely high temperatures. In this respect, if sufficient heat and oxidation resistance could be imparted to the nano particles, it would be possible to further enhance their functions. While researching more functional nano particles, we came across induction-field-activated

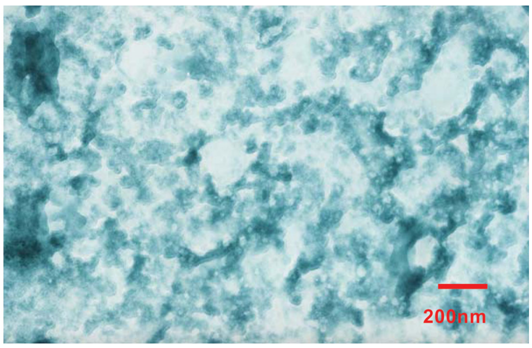


Fig. 1 Nano particles in tire

self-propagating high-temperature synthesis whereby a certain metal is added to carbon black to obtain a new compound without changing the original form of the carbon black (a process invented by Manshi Ohyanagi, professor at Ryukoku University) (**Figs. 2 and 3**).[5-8]

The nano particle (hybrid graphite black: HGB) that is obtained from carbon black by the above process retains the original form of the carbon black even after synthesis. It is possible to manufacture HGB with widely varying concentrations of B_4C and SiC, etc.[9, 10] For example, HGB containing trace amounts of B_4C showed much better oxidation resistance than a mixture of B_4C and carbon black available on the market (**Fig. 4**). The metals added during synthesis also vary widely, and it is possible to produce various types of compounds, such as SiC and TiC, through such synthesis. HGB, which is made up of nano particles containing a compound with a high melting point of 2,000°C or more, also helps to improve the corrosion resistance and mechanical strength of refractories.

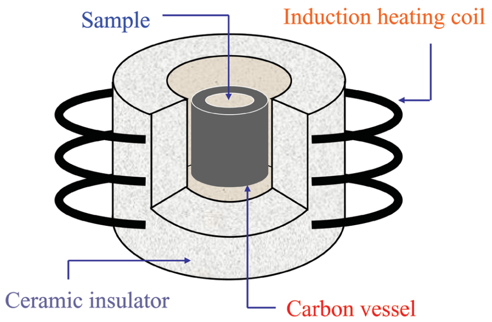


Fig. 2 Induction field activated self-propagating high-temperature synthesis

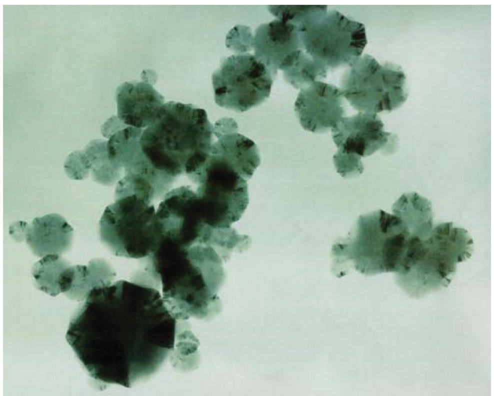


Fig. 3 TEM image of HGB with B_4C

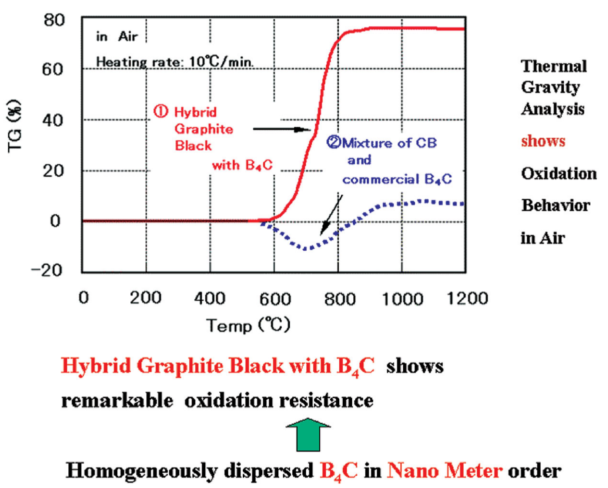


Fig. 4 TGA of ① hybrid graphite black with B_4C and ② mixture of CB and commercial B_4C

2.2.2 Nano structural matrix

An outline of the nano structural matrix is shown in **Fig. 5**. The nano structural matrix is added to the ordinary matrix of a refractory to enhance its functionality.[11] Although the amount added is only about 2 wt%, the nano structural matrix resides in the grain boundaries and significantly improves the performance of the aggregate of particles. The optimum amount of addition of nano structural matrix varies according to the overall particle size distribution, etc., and can be over 2 wt%. The nano structural matrix consists of the addition of nano carbon particles and a consolidated organic binder formed in the process of reaction/carbonization that takes place when the organic binder is heated.

In terms of the nano carbon particles added, there are two types of carbon black—the single-sphere and aggregate types. In addition, there is HGB made from carbon black using the induction-field-activated self-propagating high-temperature synthesis as mentioned above. As an HGB-applied product, graphite black that contains trace amounts of metallic components and which is similar in structure to graphite is also available. The consolidated organic binder undergoes a change in its molecular structure during the heating process and continues to be carbonized.

As an organic binder, a suspension-type binder in which nano carbon particles are dispersed was also prepared. A hybrid binder (HB)—which has carbon black added—and a high-performance hybrid binder (HHB), in which HGB is dispersed, have also been developed. These are selectively used for specific purposes. The HHB in which oxidation-resisting HGB is dispersed effectively increases resistance to oxidation at high temperatures. In the series of reactions of organic binders, we identified the possibility of forming various microstructures, which play an important part in the nano structural matrix.

The effects of the nano structural matrix are shown schematically in **Fig. 6**. As the view of an aggregate of particles with a wide grain-size distribution is enlarged, it can be seen that the voids between particles are packed with fine particles. Shown here is an example of the addition of carbon black. Generally speaking, the single-sphere type often contributes to making the packing structure denser. The aggregate type improves thermal shock resistance and heat insulation of the refractory since it reduces the elasticity, segments the

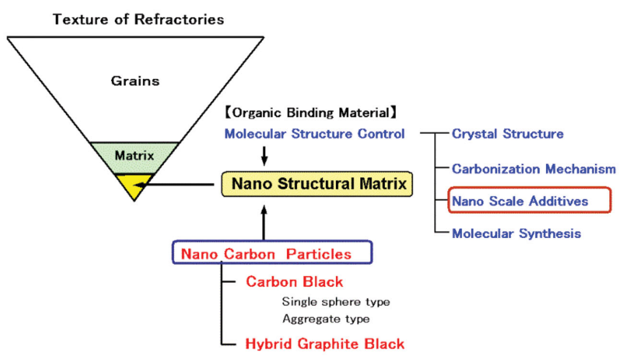


Fig. 5 Outline of nano structural matrix

pores, while increasing the number of pores, and so on. Thus, the effect of the anisotropic shape of the aggregate type can be seen.

Fig. 7 shows transmission electron microscopy (TEM) images of the representative types of carbon black: single-sphere type (A), aggregate type (B), upgraded version of aggregate type (C) and an aggregate type (D) whose properties are between those of A and C. The principal characteristics of these four types of carbon black are shown in **Table 1**.

2.2.3 Test production and verification of nanotech refractory

An MgO-C based nanotech refractory with a nano structural matrix was manufactured experimentally. Concerning the carbon, we aimed for a carbon content of no more than 5%—preferably 3% or less—from the standpoint of reducing the consumption of high-purity flaky graphite which is decreasing in supply and increasing in price, imparting good heat insulation to the refractory (an effective means of saving energy and protecting the furnace shell), and minimizing the carbon content of the refractory (this is desirable when it comes to handling low carbon steel).

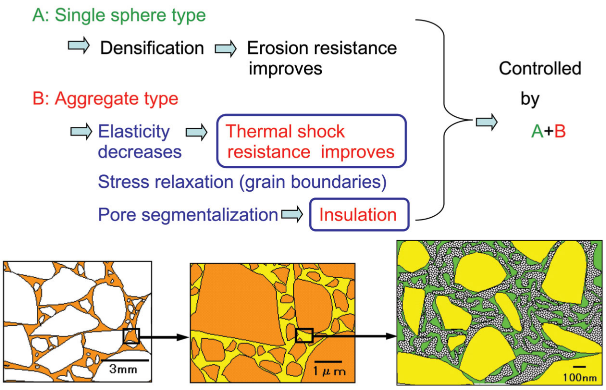


Fig. 6 Effect of nano structural matrix

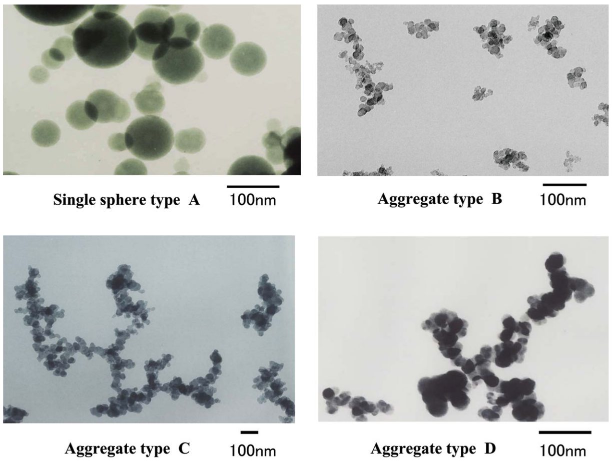


Fig. 7 TEM image of carbon blacks

(1) Test production of MgO-C based nanotech refractory aiming for 3% total carbon

As a refractory that affords good resistance to high temperatures and a long service life, MgO-C refractory is used in many converters. It contains graphite with high heat conductivity, has excellent thermal shock resistance, and is hardly wetted by molten slag (meaning that the refractory has good corrosion resistance as well). MgO has excellent corrosion resistance against molten steel and alkaline slag. Because MgO is an oxide, it also displays good heat insulation. Graphite has a number of strong points. On the other hand, it has several weaknesses too. Here are three examples. First, in the presence of oxygen, graphite is easily oxidized into CO_2 at high temperatures. Second, since graphite has high thermal conductivity, it obviously has inferior heat insulation and tends to dissipate energy easily. Third, when the furnace shell becomes excessively hot, the graphite contained within the refractory causes the refractory to deform and thus weaken.

Although a sufficient coating of slag on the refractory surface improves the oxidation resistance of the refractory, using a refractory which contains a considerable proportion of carbon in a converter is problematic because of the large amounts of oxygen blown into the converter. In recent years, there has been a tendency to increase the graphite content up to about 25% in order to further improve the thermal shock resistance of the refractory. However, problems have arisen from such an excessive proportion of graphite. Besides, the price of high-purity flaky graphite has been rising due mainly to the fact that this type of graphite is only produced in a few parts of the world and that the industrial process for graphite purification requires suitable measures to control environmental pollution. In view of the need to save energy, conserve natural resources and tackle environmental problems in the future, it is considered absolutely imperative to reduce the amount of graphite added and develop low-carbon refractories.

In the present project, we aimed to develop an extra-low-carbon MgO-C nanotech refractory with about 3% total carbon, including the carbon contained in the organic binder used. First, with the aim of examining the effects of various types of carbon black (nano particles), refractory specimens with the mixing ratios of single-sphere type A and aggregate type C varied as shown in **Table 2** and added to a suitable amount of binder were prepared. After the specimens were subjected to heat treatment (at 800℃, 1,000℃, 1,100℃and 1,400℃ for 5 hours), their physical properties were measured.

Table 1 Characteristics of carbon black

	Single sphere type	Aggregate (small diameter type)	Aggregate (comparatively uniform diameter)	Aggregate (coexistence type of large diameter and small diameter)
Carbon black species	A	B	C	D
Specific surface area (iodine adsorption: mg/g)	19	200	60	20
DBP absorption (ml/100g)	30	130	130	140
Component particle diameter (nm)	90nm class	10nm class	40nm class	-
Feature	Surface area: small Oil adsorption: small	Surface area: large Oil adsorption: large	Surface area: medium Oil adsorption: large	Surface area: small Oil adsorption: large

Table 2 Experimental condition of experimental brick (%)

Specimen	CB1	CB2	CB3	CB4	CB5
MgO	95	95	95	95	95
Single sphere type A	2.0	1.5	1.0	0.5	0.0
Aggregate type C	0.0	0.5	1.0	1.5	2.0

The measurement results are shown in **Fig. 8**. The addition of single-sphere type A alone shows a marked tendency to increase both the strength and elasticity. When the mixing ratio of aggregate type C is 0.5% or more, the modulus of elasticity decreases to about half, although the strength declines slightly. In this case, therefore, it can be expected that the thermal shock resistance (spalling resistance) will improve. The heating temperatures of 800℃ and 1,000℃ make a significant difference. Since the specimen structure stabilizes when the heating temperature is around 1,000℃, it is desirable to use the refractory after it is subjected to heat treatment at 1,000℃ or higher.

On the basis of the above results, we made some experimental bricks (specimens X and Y in **Table 3**). Specimen X was prepared by adding single-sphere type carbon black, which effectively increases the refractory's density, and aggregate type C carbon black—which improves the thermal shock resistance of the refractory. Carbon black type D used in Specimen Y is a hybrid of A and C. Specimen Z, a conventional brick available on the market, was used for comparison. The total carbon in X and Y, respectively, is 3% (flaky graphite 0%, carbon black 1.5%), whereas that of Z is 20% (flaky graphite 18%), more than six times greater.

In a spalling test, Specimens X and Y showed spalling resistance comparable to that of Specimen Z, despite the fact that the carbon content of X and Y was only about one-sixth that of Z. Thus, by using carbon black appropriately, it is possible to impart excellent spalling resistance to the brick.

In addition, as shown in **Fig. 9**, the heat conductivity of Specimens X and Y, which contain no graphite, is about one-seventh that of Specimen Z and hence, X and Y display high thermal insulation performance.[12)]

Fig. 10 shows examples of the results of a corrosion resistance test of the specimens carried out on the slag line of an actual ladle. It can be seen that the wear rates of Specimens X and Y containing 3% carbon are low compared with that of Specimen Z.

The nano carbon particles shown in Fig. 5 are carbon black and hybrid graphite black (HGB). When dispersed evenly in the refractory, HGB permits controlling the binding strength effectively even if the amount added is extremely small. In addition, since the resulting carbides, such as B_4C and SiC, have good reactivity, HGB imparts excellent oxidation resistance to the refractory.[13)] In Specimen B in **Table 4**, the 1.5% HGB added in the form of particles and the small amount of HGB contained in HHB show excellent oxidation resistance in a high temperature oxidizing atmosphere. It is assumed that once a thin oxidized layer is formed on the refractory surface,

Table 3 Effect of addition of aggregate types (%)

Specimen (MgO-C(3%))	X	Y	Z(conventional)
MgO	96	96	78
Single sphere type A	1.0	0	0
Aggregate type C	0.5		0
Aggregate type D	0	1.5	0
Flake graphite	0	0	18
Resin binder	2.5	3.2	2.8
Spalling test (*1) cycle	12	15	15

(*1) cycles until peeling occurs by repetition of dipping specimen in molten iron at 1400℃

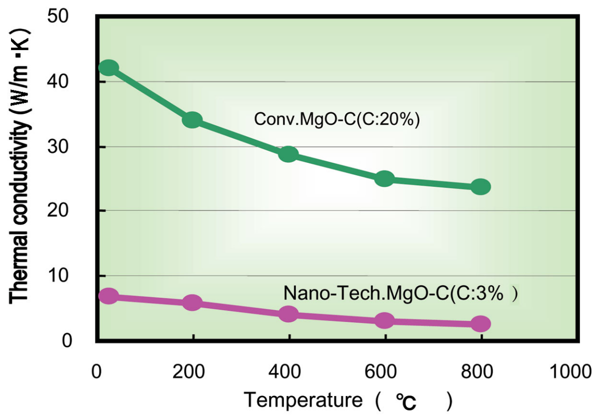


Fig. 9 Thermal conductivity of MgO-C bricks

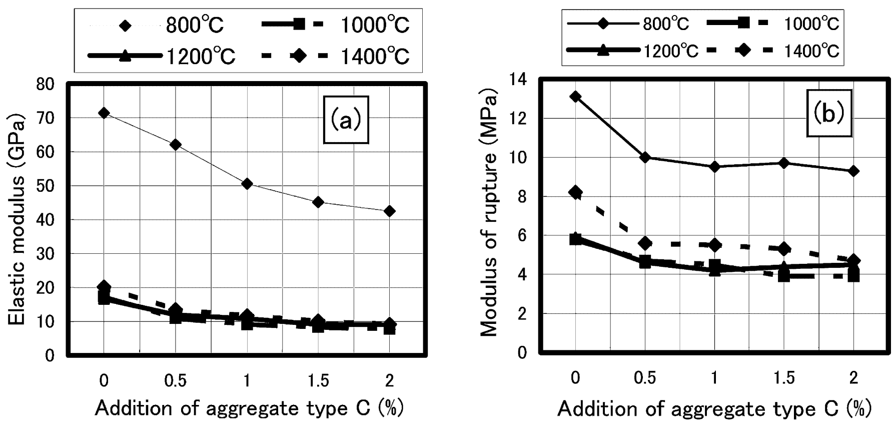


Fig. 8 Additional effect of aggregate C type

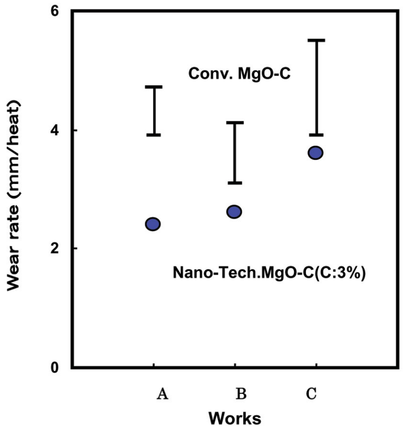


Fig. 10 Performance of nanotech MgO-C brick applied to practical use

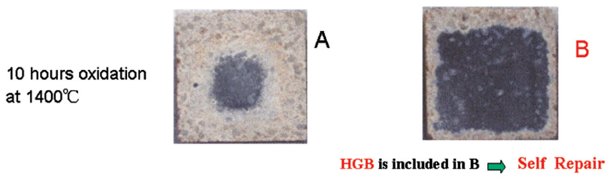
Table 4 Effect of HGB on oxidation resistance

"Oxidation Resistance"

Specimen (MgO-C(3%))	A	B
MgO	96	96
Aggregate type	1.5	1.5
Resin binder (HB)	3.2	
Resin binder (HHB)		3.2

Small quantity

Hybrid Graphite Black



the pores close in the refractory as a result of appropriate sintering progress. Since the refractory is not oxidized any more even when it is reheated, it is considered that the refractory has a self-repairing function.

The textures of nano structural matrices were observed under a field emission scanning electron microscope (FE-SEM). **Fig. 11** (a) shows an FE-SEM image of the texture of Specimen X shown in Table 3. Fig. 11 (b) shows an enlarged view of the image shown in Fig. 11 (a). It can be seen that particles tens of nanometers in size are dispersed in the specimen.

Fig. 12 and 13 show parts of the organic binder in the nano structural matrix that was carbonized by heating.[14] The lacelike or fibrous (whisker-like) structure shown here is conspicuous when the refractory is heated to 1,000℃ or higher. As shown in Fig. 8, there was a marked difference between heating at 800℃ and at 1,000℃. Specifically, when the refractory was heated to 1,000℃, its elasticity decreased noticeably.

Since the formation of a lacelike or fibrous structure is conspicuous when the refractory is heated to 1,000℃ or higher, we consider that the formation of such a structure in the nano structural matrix is one factor accounting for the excellent thermal shock resistance of this nanotech refractory. Like the fibrous (lacelike) products, the clusters of aggregate type carbon black are anisotropic. It is considered, therefore, that the formation of a structure resembling those anisotropic substances intertwined with one another effectively improves the thermal shock resistance of the refractories. We feel confident

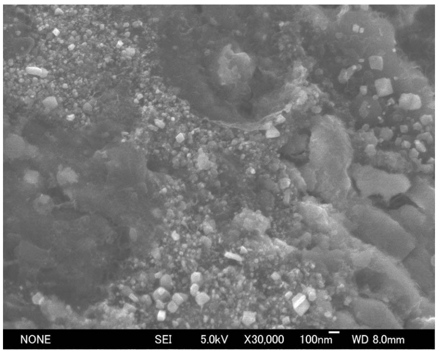


Fig. 11 (a) FE-SEM image of Nano structural matrix of specimen X in Table 3

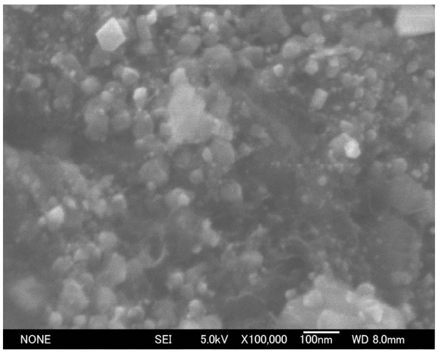


Fig. 11 (b) Enlargement of Fig. 11 (a)

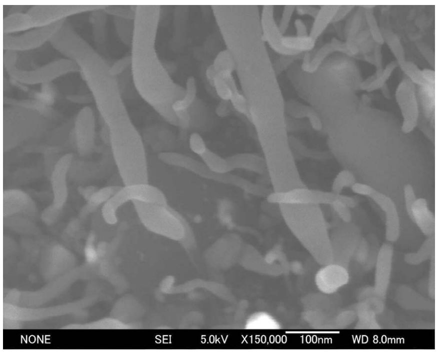


Fig 12 Lace like structure in carbonized matrix

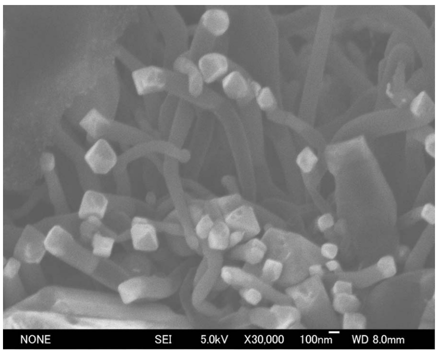


Fig. 13 Fiber like structure in carbonized matrix

that controlling the dispersion of nano particles and the nano structural matrix formed by products of carbonization and other reactions is a key technology for next-generation refractories.

The results of a composition analysis of a fibrous structure, like the one in Fig. 13, are shown in **Fig. 14**. The heads of the fibers differ in brightness. An Energy Dispersive X-ray (EDAX) analysis revealed that they contained Al, O, and Mg, etc. Therefore, we assume that the fibers are Al-O or Al-Mg-O based products, although we hesitate to say that positively because of the accuracy of the analysis. Since a small amount of Al is added in the brick manufacturing process, it is also estimated that the formation of a fibrous structure is promoted in the organic binder carbonization process as the fusion, evaporation, solidification, etc. of Al occur and some catalytic functions apply. At present, we are studying ways to control the formation of those fibrous products in the nano structural matrix.

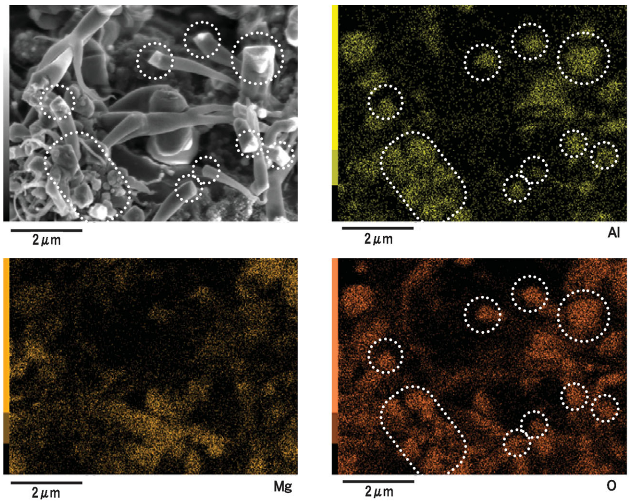


Fig. 14 Composition analysis of fiber like structure

(2) Variations of MgO-C based nanotech refractory

In the preceding section, we described the circumstances that led to the development of low-carbon MgO-C nanotech refractories having 3% total carbon. In the latter part of that section, the importance of the heat treatment process was discussed. Now we have three versions of nanotech refractories which can be used for specific purposes in specific fields.

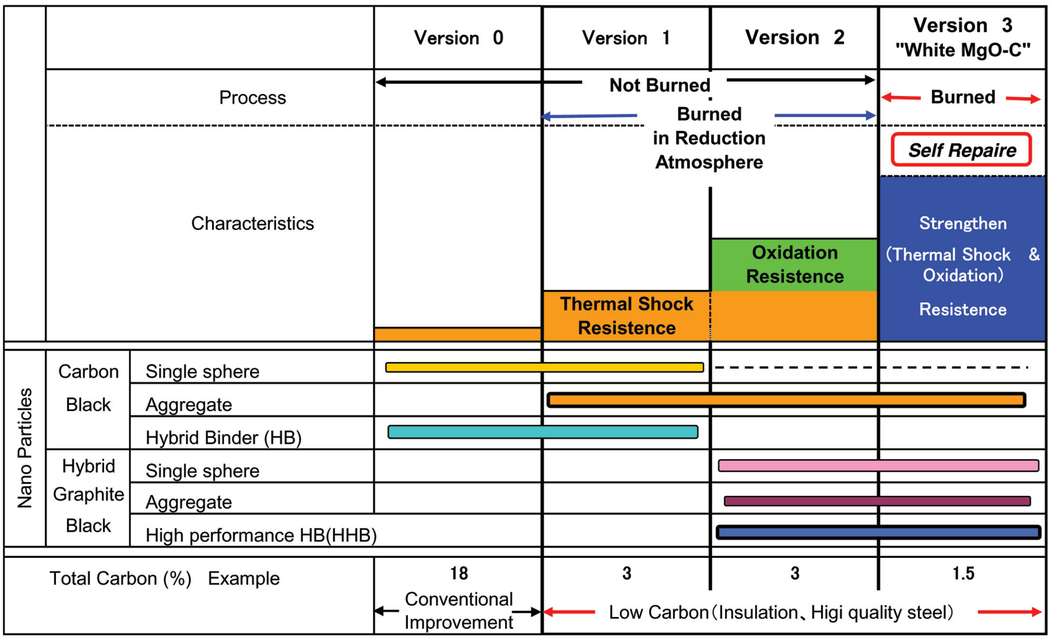
These are shown in **Table 5**. Versions 1 to 3 represent the region of nanotech refractories. Version 1 applies aggregate carbon black to improve the thermal shock resistance of low-carbon refractories. Version 2 applies HGB to permit controlling the intensity of sintering and improve oxidation resistance under high temperatures. Both Version 1 and Version 2 are available in two types—the non-fired type that is used after baking and the fired type that is used in a reducing atmosphere.[15] As already mentioned, our research also emphasizes the organic binder heat treatment process. Specifically, controlling the structure of the nano structural matrix is studied. The fired type shows stable physical properties and offers good resistance to thermal shock.[16] Version 3 is an MgO-C nanotech refractory of a fired type whose surface is white. Otherwise called "white magnesia carbon," this nanotech refractory is described in the following section.

(3) Development of white magnesia carbon (WMC)

WMC is an MgO-C nanotech refractory on which a thin, white rim layer as shown in **Fig. 15** is formed by a heat treatment process in which the atmosphere and heating rate are carefully controlled.[17-19]

The total carbon in WMC after heat treatment is about 1.5%. Thus, it may be said that WMC is an MgO refractory containing a very small amount of carbon. Concerning the thermal shock resistance evaluated by the number of times each specimen was dipped into 1,400℃ hot metal, WMC was inferior to an ordinary MgO-C refractory with about 20% total carbon (18% graphite), 8 times vs. 15 times or more. With respect to its corrosion resistance evaluated by a test at the slag line of an actual ladle, however, WMC proved better, with the wear rate being about half that of ordinary MgO-C refractories (**Fig. 16**).

Table 5 Evolution of MgO-C nanotech refractories



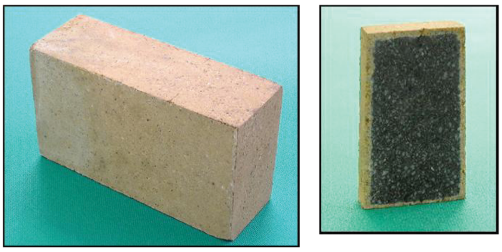
In addition, the joints of WMC coated with a thin layer of high-purity MgO mortar were sintered with the MgO rim layer on the surface of the WMC to form high-purity MgO after the WMC was used, thereby showing good corrosion resistance.

One salient feature of WMC is its oxidation resistance under high temperatures. **Fig. 17** shows examples of the oxidation behavior of WMC under high temperatures. A corner was cut out from a WMC refractory and subjected to oxidation tests under high temperatures in the atmosphere. In an oxidation test at 1,000°C, the oxidized layer of the part other than the rim layer grew as thick as 12 mm. On the other hand, in an oxidation test at 1,400°C, the oxidized layer of the part other than the rim layer was as thin as about 3 mm. Even when the same specimen was again subjected to an oxidation test at 1,000 °C, the thickness of the oxidized layer remained at 3 mm. When the interior of the WMC is exposed to the hot face and is oxidized at a temperature of around 1,000°C, there are cases in which the oxidized layer increases in thickness. However, when the WMC is exposed to temperatures of 1,400°C or higher, it forms a thin, dense rim layer of MgO on the surface and thereby shows excellent oxidation resistance against temperature changes that occur subsequently. We consider that the WMC displays excellent oxidation resistance thanks to what may be called a self-repairing function; that is, the

composition	amount(%)
MgO	96
HGB Aggregate type	0.4
Binder HHB	2.5
Others	1.1

HGB:Hybrid Graphite Black

HHB:High performance Hibrid Binder



Appearence   Cross Section

Fig. 15 White MgO-C nanotech refractories (WMC)

	WMC	Joint of WMC	Conventional
Total Carbon(%)	1.5		20
			
	Horizontal cross section	Vertical cross section	Horizontal cross section
Wearing rate (mm/heat)	2.3		4.1

Fig. 16 Test result at the slag line of the ladle

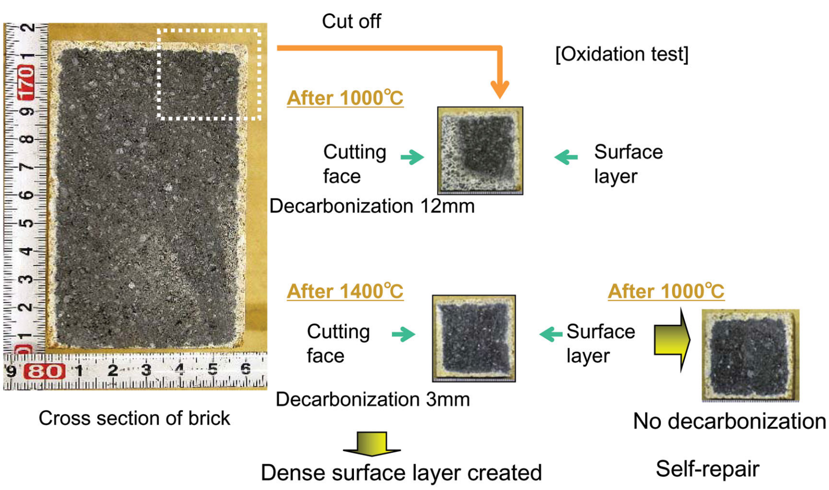


Fig. 17 Oxidation resistance of white MgO-C nanotech refractories

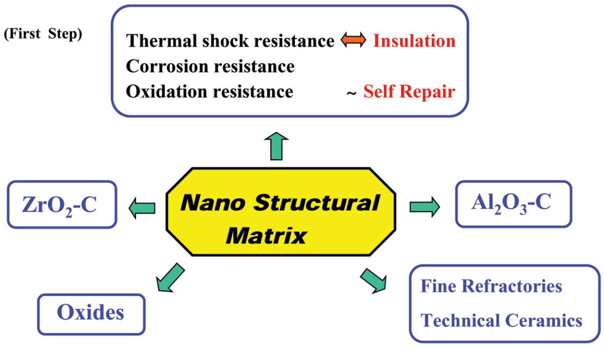


Fig. 18 Application of nano structural matrix to ceramic materials

oxidation resistance of HGB contained in the WMC in trace amounts and the formation of a rim layer with minimal gas permeability by control of the sintering of MgO.

(4) Expansion of application of nano structural matrix

We have so far described the development of nanotech refractories using an MgO-C-based brick as an example.[20, 21] The key technology for nanotech refractories is the nano-structural matrix. As shown in **Fig. 18**, the application of this key technology is being expanded to various fields, with MgO-C-based material as the first step.[22]

The key technology that was first applied to MgO-C-based refractories for refining furnaces is also being applied to Al_2O_3-C- and ZrO_2-C-based nanotech refractories for continuous casters.[23, 24] At the same time, a nano structural matrix for oxide-based refractories is being developed.

3. Outlook for Nanotech Refractories in the Steel Industry

Looking at thin steel products, typified by automotive sheet, increasing efforts have been made to develop lighter, stronger steels as part of our measures to conserve natural resources and save energy. Concerning thick steel products, weatherproof plates for unpainted bridges, corrosion-resistant plates for gigantic container vessels, and pitting corrosion-resistant plates for oil tankers are increasingly demanded. Pipelines to transport natural gas, which is attracting growing attention as a source of clean energy, are required to have high strength, low-temperature toughness, field weldability and sour resistance (i.e. resistance to hydrogen-induced cracking and sulfide-stress corrosion cracking). Thus, there is strong demand for high-strength, high-toughness steel plates.

For shapes and bars, such as steel cord, absolute cleanliness is vital to completely ensure wires do not break due to the presence of nonmetallic inclusions in the drawing process. As the quality requirements for steel products have become increasingly stringent, so there has been a marked change in conventional steel-refining processes. With respect to the refractories used in the refining and casting processes, too, extra-low-carbon or carbon-less bricks, which allow for strict control of molten steel composition, remain the goal. Thus, it is indispensable to develop new refractory technology that enables the manufacture of steel products which meet the above quality requirements.

On the other hand, for Japan's steel industry—which accounts for 10% of the total energy consumption of the country—it may be said that attaining the targeted energy savings based on the Kyoto Protocol is a major challenge that cannot be evaded. In the Japanese steel industry, refractories which use graphite are increasing. This is due mainly to the fact that graphite, having high heat conductivity, is often added as an effective measure to improve thermal shock resistance and reduce the occurrence of cracks. On the other hand, the addition of graphite reduces the thermal insulation of the refractories. This in turn causes the furnace shell temperature to rise and more heat to dissipate. These phenomena contradict efforts to save energy. The low-carbon MgO-C nanotech brick shown in Fig. 9 can be regarded as an MgO brick with trace amounts of carbon added. Since the heat conductivity of this brick is about one-seventh that of conventional MgO-C bricks, it contributes to enhanced thermal insulation.

Japan imports some 37% of the raw materials it needs for refractories. In view of the hike in prices of domestically produced raw materials for refractories, the country now imports most of the principal raw materials—fused magnesia and graphite—from China. In order that China does not aggravate its environmental pollution and is able to secure its natural resources on a long-term basis, it seems that the abolition of refunding value-added taxes and the introduction of new import duties that China imposed last year are, in a way, inevitable consequences of the current circumstances. Under those conditions, in order for Japan to create technology for differentiation without depending on raw materials that only exist locally, it is considered indispensable to promote the utilization of seawater magnesia (this was formerly used in large quantities) and widen the choice of raw materials (e.g. coarse particles) through R&D on nanotech refractories whose matrix structure is controlled in the order of nanometers as described earlier.

This chapter describes an example in which a magnesia brick with a nano structural matrix was used in degassing equipment from the standpoint of the recent quality requirements of steel products, environmental measures, saving energy and effective utilization of available natural resources.

We test-manufactured MgO-C nanotech refractories using ordinary phenol resin and HGB-dispersed resin (HHB) as the binder. The basic composition of Specimen No. 1 is shown in **Table 6**.

Fig. 19 shows the X-ray diffraction pattern of an MgO-C nanotech brick (Specimen No. 1). Despite the fact that no graphite was mixed in the specimen, relatively intense diffraction peaks of graphite were observed. It is assumed that this graphite was derived from the carbon contained in the phenol resin binder.

Fig. 20 shows an SEM image of the fracture surface of Specimen No. 1 after it was subjected to reduction-firing in coke grains at 1,000 ℃ for six hours. It can be seen that the specimen has a scaly structure. This small scaly structure seems to have something to do with the crystallization of carbon derived from the resin in the matrix.

Using Specimen No. 1 as the base, we prepared another specimen (Specimen No. 2), to which was added a trace amount of HGB, and applied it to the lower side walls of Ruhrstahl-Heraeus (RH) degassing equipment. The principal properties of Specimen No. 2 are shown in **Table 7**. Looking at its mechanical properties, the change in modulus of static elasticity between 600℃ and 1,400℃ is small

Table 6 Basic compositions of nanotech refractory brick

Specimen	No.1
Carbon black (see also Fig. 7)	D
Resin binder	HHB
Additives	Al
Flake graphite	None

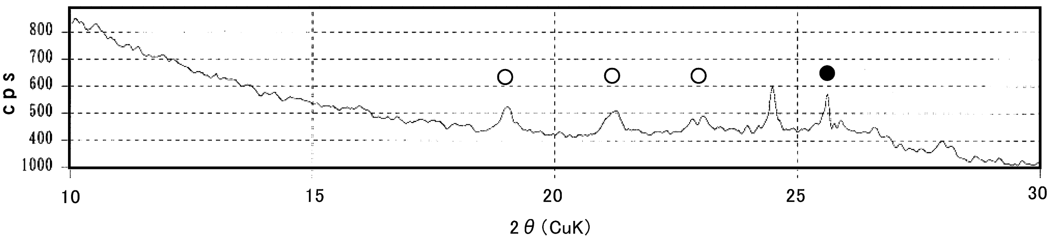


Fig. 19 XRD patterns of a No.1 nanotech magnesia carbon brick after firing at 1,000℃
Open circles show peaks of B_4C, and closed circles shows peaks of graphite. Horizontal axis shows 2 θ using copper target, and vertical axis shows intensity respectively.

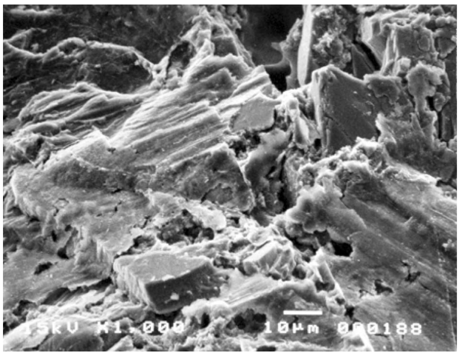


Fig. 20 SEM image of fracture surface of No.1 nanotech magnesia carbon bricks after firing at 1,000℃

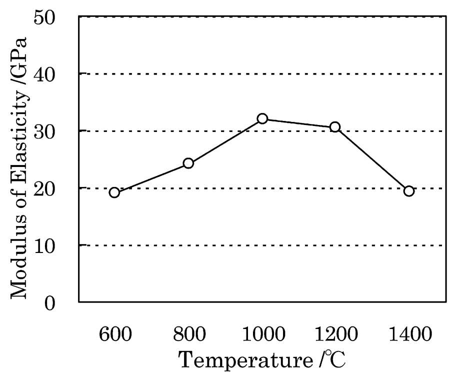


Fig. 21 Modulus of static elasticity of No.2 nanotech magnesia carbon brick

Table 7 Properties of the No.2 nanotech magnesia carbon brick after firing at 1,400℃

C (mass%)	3.5
Bulk density	3.13
Apparent porosity (%)	7.3
Modulus of rupture at 1,400℃ (MPa)	24.9

as shown in **Fig. 21**. In particular, the modulus of static elasticity remains almost the same between 1,000℃ and 1,200℃. Probably the reason for this is that the HGB contained in the binder and the very small amount of HGB added to the specimen restrained the sharp change in modulus of static elasticity that normally occurs at around 1,200℃. We estimate that although Specimen No. 2 contained no graphite and its carbon content was very small, the addition of HGB promoted the crystallization of carbon derived from the phenol resin binder and the control of sinter strength improved the thermal shock resistance.

Fig. 22 shows the appearance of the MgO-C nanotech brick (Specimen No. 2) after it was used in RH degassing equipment. The specimen showed better corrosion resistance than conventional MgO-C bricks, with very little spalling.

As described above, it was confirmed that our magnesia brick with a nano structural matrix could be used for actual furnaces and that its functions could be further enhanced in the future.[25, 26] We expect that this technology will find many applications in the future, including carbon block for blast furnace bottoms, taphole mudding material and monolithic runner material, as well as fired and non-fired bricks (e.g. Al_2O_3-SiC-C bricks for mixer cars, MgO-C bricks for converters, and Al_2O_3-MgO-C bricks for ladles) and fired Al_2O_3-C bricks which are already used for nozzles (sliding gates, long nozzles, immersion nozzles) for continuous casting.

Fig. 22 No.2 nanotech magnesia carbon brik in a RH degsser sidewall after use (between broken lines)

4. Conclusion

We have described the application of nanotechnology as an effective means of achieving a breakthrough in R&D on refractories. The key point of the nanotech refractories described in this report is the nano structural matrix comprised of (1) nano particles, such as nano carbon particles and hybrid graphite black (HGB) manufactured by induction-field-activated, self-propagating, high-temperature synthesis, and (2) a unique bond structure obtained by controlling the organic binder carbonization process.

By significantly improving the brick's thermal shock resistance through effective utilization of aggregate-type nano carbon particles and by controlling the brick density through use of nano carbon particles of the single-sphere type together with aggregate type nano carbon particles and controlling also the bond structure formed by an organic binder and active HGB which produces carbides, etc., we have developed a high-function, extra-low-carbon MgO-C nanotech brick (carbon content less than 3%) with excellent resistance to thermal shock, corrosion and oxidation. This new brick is being applied in various steelmaking processes. In the future, we would like to see it applied more widely—not only in the steelmaking processes, but also in the fields of resources, energy, the environment, etc. to help establish a sustainable society.

The creation of a nano structural matrix is considered to represent a bridge between two stages—that of macrostructure control and microstructure control of refractories. By securing the diversity of pore structure (number of pores, pore size, pore shape) and controlling the bonds between particles appropriately, we intend to help attain simultaneously both thermal shock resistance (low strength, coarse structure) and corrosion resistance (high strength, dense structure), which have hitherto been considered to be incompatible with each other.

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Shinichi TAMURA
Executive counselor & chief researcher, Japan Technical Information Services Corporation; research supervisor at Nanotech Refractories Institute (nonprofit research institute founded in 1999), former general manager of Fine Ceramics Application & Development Department, Plant Engineering & Technology Bureau, Nippon Steel Corporation
3-25-23, Takanawa, Minato-ku, Tokyo

Taijiro MATSUI
General manager of Refractory Ceramics R&D Div. of Environment & Process Technology Center

Tsunemi OCHIAI
Former general manager of Hirohata Refractories Development Department, Plant Engineering & Technology Bureau; founder and representative of Nanotech Refractories Institute since its foundation in 1999

Kiyoshi GOTO
PhD; chief researcher of Refractory Ceramics R&D Div. of Environment & Process Technology Center