Progress and Perspective of Refractory Technology

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Abstract

Efforts have been made to enhance refractory technology to support stable production of high-quality steel at low costs. This is true especially in the field of steelmaking, where refractories are used heavily. The service life of MgO-C bricks for converters has been extended by use of high-purity materials and new additives and the development of a low-graphite type excellent in spalling resistance. For secondary refining vessels and molten steel ladles, monolithic refractories have come to be used widely. In continuous casting, measures to prevent the clogging of submerged entry nozzles (SENs) have been developed on the basis of a study of its mechanisms, and anticorrosion material for the powder line of SEN has advanced. New refractory repair methods suitable for different applications, combined with diagnosis systems, have been developed to enhance the quality and accuracy of repair work.

1. Introduction

Refractories are indispensable for steel production; they constitute essential part of the steel production process, and have significant influence on the production costs. Refractory technology has developed together with steel production technology, supporting its advance. The quantity of refractories used in steelmaking processes accounts for no less than two thirds, approximately, of the total used for integrated iron and steel production. Therefore, to extend the service life of the inner lining of ladles and reaction vessels, stabilize steel production, reduce costs, and improve product quality, it is necessary to adequately select the most suitable refractory according to the use condition. In steelmaking processes, the characteristics of molten metal, slag chemistry, atmosphere, and temperature are widely varied at different parts of reaction vessels or ladles, and therefore, the functions required for refractories differ significantly. Thus, the properties of refractories for different applications must be designed delicately in consideration of the use conditions. The present paper outlines the development and improvement of refractories for the reaction vessels and ladles for steelmaking processes, and tries to prospect the future trends in the field.

2. Progress of Refractory Technology

2.1 Refractories for converters

(1) Historical change in converter refractories

Since the role of a converter is to adjust the contents of C, Si, Mn, P, S, etc., in molten iron tapped from blast furnaces into the desired steel chemistry, the operation temperature is as high as 1,600 to 1,700°C. Because the mixture of molten oxides (slag) that are formed during converter refining under oxygen blowing is basic, refractories consisting of basic and high-melting-point oxides, namely MgO and CaO, have long been used for the inner lining of converter vessels.

In the 1960s and 1970s, dolomite refractories such as tar-bonded dolomite bricks and baked magnesia-dolomite bricks were developed and used, but they had shortcomings of rapid slaking during use and spalling due to high thermal expansion. As a solution to these problems and to obtain longer service life, dolomite-carbon bricks, and then in the 1980s, MgO-C bricks, were developed. The latter became widely applied to converters in the 1980s because they were free from the slaking of dolomite, resistance to slag attack was greatly improved because of the composite structure of magnesia and graphite, and spalling resistance was markedly improved as graphite of low thermal expansion effectively absorbed the expansion of magnesia. This means that MgO-C bricks represent an epoch-making technology in the history of refractories, wherein the resistance to corrosion (dissolution of components into slag) and that to spalling, the long-standing and mutually opposing requirements for refractories, were markedly improved at one stroke, one of the achievements that the refractory industry of Japan may justly be proud of.

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Various measures have been worked out since the 1990s to extend the service life of MgO-C bricks in response to the requirements for longer converter campaigns. Typical improvements include suppression of graphite oxidation during furnace operation by addition of metallic Al, Al-Mg alloys, and borides such as B$_2$C and CaB$_6$, and greater resistance to slag attack by purification and use of coarse crystallized magnesia and purification and use of large grain graphite.\textsuperscript{2-4}

(2) Orientation of future development of converter refractories

The orientation of future development of converter refractories is outlined here in consideration of the business environment of the steel industry and the requirement for longer service life.

Presently, most of the MgO-C bricks for converters in Japan are imported from China. Domestic bricks are used on the tapping-side wall, etc., where the use condition is very tough and long service life is required. In the meantime, the demand for Chinese graphite for electronic applications has increased, and as a consequence, the price tends to go up, and depletion of high-quality graphite resources is being feared. On the other hand, heat loss through converter refractories and the shell has long been a problem, but no substantial measures have been proposed to decrease it.

In consideration of these problems, emphasis will have to be placed on the following points in the development of converter refractories: longer service life, decrease in graphite content, decrease in thermal conductivity, resource saving, and promotion of material recycling. To meet these requirements, Nippon Steel Corporation has started the development of low-graphite MgO-C bricks.

The target in the development is to decrease the content of graphite from conventional 15%-20% to 10% or less. While thermal conductivity naturally decreases when the graphite content is lowered to two-thirds or a half, what is important is to improve the corrosion resistance of MgO-C bricks even with the lower graphite content, without sacrificing their excellent spalling resistance. For this, it is important to make the structure denser while maintaining the spalling resistance. Nippon Steel Corporation has aimed at improving corrosion resistance by making the structure denser, namely decreasing porosity, and at maintaining the spalling resistance, and has focused on carbon black nanoparticles as a promising material.\textsuperscript{1,4}

Fig. 1 is a photomicrograph through a transmission electron microscope (TEM) of nanosized particles of carbon black used for new bricks that the company is developing. Here many carbon black particles up to several tens of nanometers in size form a large aggregate. Fig. 2 is a photograph taken at an evaluation test of newly developed low-graphite MgO-C bricks, to which a small amount of nanoparticles was added. The bricks were laid at a wall position inside the trunnion of a commercially operating converter. The developed bricks proved superior in terms of durability to conventional high-graphite MgO-C bricks (containing 18 mass% graphite). Further tests of the new low-graphite bricks are being conducted, and the orientation for the development of the low-graphite MgO-C bricks will be defined on the basis of the test results.

2.2 Refractories for secondary refining processes

Some of the steel refining functions that were conventionally carried out in converters or electric arc furnaces were separated and came to be performed as finishing steps after the tapping from those furnaces; these are called secondary refining processes. Vacuum degassing by the DH or RH method began in the 1950s for removing hydrogen gas from molten steel, and then VOD, AOD, and other secondary refining facilities were developed and used industrially. More recently, functions to blow in oxygen, argon, or flux powder were added to secondary refining equipment for accelerating decarburization, heating steel by burning aluminum, removing sulfur, etc. As a result, the use condition of the refractories became increasingly severe. In contrast to other refining processes, refractories for secondary refining must work stably under vacuum, since most secondary refining processes progress under such a condition.

For this reason, basic magnesia-chrome bricks have long been used for secondary refining facilities. Magnesia-chrome bricks are divided into three types according to the materials used: direct bonded bricks mainly made of magnesia and chrome and fired at a high temperature; semirebonded bricks made likewise except that about 50% of fused magnesia-chrome (mixture of magnesia and chrome, melted in an electric furnace) is added; and rebonded bricks made only of magnesia and fused magnesia-chrome. Additionally, a new type of fired magnesia-chrome bricks with an addition of chromium oxide\textsuperscript{10} was developed, aiming at higher corrosion resistance. All these varieties of magnesia-chrome bricks are applied to different parts of secondary refining vessels according to their characteristics.

The latest trends in this field have been elimination of chromium; use of MgO-C bricks\textsuperscript{11}; and wider use of monolithic, or castable, refractories. In 1996, Nippon Steel Corporation introduced the microwave hot-air dryer and began to use castable refractories for the lower RH treatment vessel at Oita Works as the first case in the world.\textsuperscript{12} Kimitsu Works also expanded the application of castable refractories actively, and began to use alumina-spinel castable and alumina-magnesia gunning refractories for various applications.\textsuperscript{13} A method of repairing locally damaged wall areas in hot to extend ves-
sel campaign life was applied to RH facilities. Typical repair methods using monolithic refractories include dry gunning to spray magnesia, dolomite, etc., in hot; flame gunning; and injection repairing, whereby dummy cores are placed inside the lower vessel or a snorkel (immersion tube) and paste of alumina-magnesia refractory is pumped in.

Measures such as continual use of one lower vessel (instead of alternate use of two) and intensive heat retention of the vessel between treatment batches are taken to extend the campaign life of RH lower vessels. A snorkel is lined with bricks on the inner wall and alumina-magnesia monolithic refractory on the outer, but deformation of the steel core often causes cracks on the outer lining. Fog cooling of the core was recently introduced, whereby water in mist 10 µm or less in mean size is sprayed onto the hollow core surface to suppress its deformation. The vessel campaign has been extended to 1000 charges or more for different use conditions and repair methods, changes in operation conditions, structural changes of steel cores/shells, etc.

2.3 Refractories for steel ladles

Conventionally, the main lining material for molten steel ladles was high-silicate bricks, but as the process route via secondary refining and continuous casting became increasingly dominant in the 1960s and thereafter, the use condition of the ladles grew increasingly severe, and in response, high-silicate bricks were replaced by zircon bricks. Then, against the backgrounds of wider use of castable refractories that began around 1970 for mechanizing refractory work and labor saving, and elimination of silica from refractories for high-purity steel production, alumina-spinel castable refractory was developed in the late 1980s.

As the alumina-spinel castable refractory became the main lining material of the ladles, there arose the need for decreasing the use of lining materials at intermediate repairs and increasing the interval between major lining changes. When alumina-spinel castable refractory is used for ladles, it wears at the wall portion because of structural spalling caused by slag penetration, as well as at the bottom portion because of the said structural spalling, arching, and cracking caused by expansion due to thermal stress in the lining. Alumina-magnesia castable refractory was developed as a measure against the above wear of alumina-spinel castable refractory.

Alumina-magnesia castable refractory is significantly different from alumina-spinel castable refractory in terms of the manner of thermal expansion and thermal stress. According to the thermal expansion curve of alumina-magnesia castable refractory, it expands rapidly in the temperature range above approximately 1,400°C, mainly because of the formation of spinel accompanying volume expansion. In contrast, according to the same of alumina-spinel castable refractory, it does not exhibit such rapid expansion.

When applied to actual steel ladles, the refractory is restricted, and the rapid expansion of alumina-magnesia castable refractory that occurs on the working surface side serves to make the refractory structure denser (smaller open pore diameter), thus preventing slag from penetrating into the lining layer. Since such large volume expansion on the working surface side does not occur with alumina-spinel castable refractory, the structure is not made denser and slag penetration is not suppressed. For this reason, alumina-magnesia castable refractory is more resistant to slag penetration and is less prone to the wear caused by structural spalling than alumina-spinel refractory.

In addition, the thermal stress curves of alumina-spinel and alumina-magnesia castable refractories clearly indicate that the maximum thermal stress of the latter is lower than that of the former, which means that the latter is less prone to the risk of arching and cracking than the former.

As stated above, alumina-magnesia castable refractory has come to be used widely for steel ladles because it is more resistant to slag penetration and has lower thermal stress than alumina-spinel refractory. Note that alumina-spinel castable refractory has become applicable to steel ladles also because of shrinkage control during sintering to decrease the risk of arching.

Nippon Steel Corporation began to use castable refractories for molten steel ladles prior to other steelmakers, and now uses it for the entire walls and bottoms of the ladles, except the slag line areas. The company also developed castable basic refractory, and with it, all the ladle inner surfaces including the slag line areas came to be lined with castable refractories.

To continue using alumina-magnesia castable refractory stably and for a long period, it is important to prevent the molten metal from penetrating into the refractory layer through cracks that may form during the use. Cracks develop in the refractory layer because of its structural change during use. It is important, therefore, to establish technology for optimum material design to prevent the structural change, on the basis of the evaluation of the sintering and creeping properties of the material at high temperatures.

2.4 Refractories for continuous casting

The development of refractory technology in the field of continuous casting has mostly been related to the teeming system, or more specifically, to submerged entry nozzles. Fig. 3 is a schematic sectional view of a common submerged entry nozzle. The number of charges of sequential casting is determined by the service life of these nozzles, which is governed by two factors: clogging due to sticking of non-metallic inclusions (oxidizing products and tundish slag) and skulls and local corrosion. These problems occur because the nozzles are made of carbon-containing refractory and are used in the molds. The measures studied and taken against these problems are explained below in more detail.

(1) Measures against sticking of inclusions

The sticking of inclusions and skulls is considered to occur depending largely on factors related to the steel grade, such as too small superheat and large temperature drop in the tundish, and therefore, it can be prevented effectively by operation improvement. Provision of heat-insulating slits on the nozzle side was proposed as a countermeasure, but this has not been widely practiced.
A widely practiced measure is argon gas blowing through the upper nozzles or the very submerged entry nozzles; it has certain effects of preventing inclusions from sticking to the nozzles and having them float to the metal surface and get caught in the slag.

Various measures have been tried to improve the quality of the material for the inner liner of the molten steel duct. Such attempts include measures to prevent the sticking of inclusions by rectifying uneven steel flow in the nozzle caused by the sliding nozzle. There was a proposal to form steps on the surface of the inner liner and another to form skewed fins on the duct wall to give twist to the steel flow.\(^{29}\)

Usually, submerged entry nozzles are made of alumina silica and graphite (hereinafter AG, refractory following the Japanese convention), which has been prone to the sticking of inclusions since the 1970s when it began to be used for the application. The reason for this is as follows: during use, silica in the AG refractory reacts with carbon of the graphite and in the resin of the binder and forms products in gas. This leads to oxidation of sol-Al in steel into alumina, and the reaction products in gas diffuse into molten steel to form concentration gradients in the laminar flow layer along the inner nozzle surface, which makes it easy for inclusions to stick to the nozzle surface. This indicates that the cause of the sticking of inclusions lies in the very AG refractory. Therefore, another sticking prevention measure is to change the material of the inner liner from the AG refractory to another that does not cause sticking easily. Fig. 4 schematically illustrates the mechanism by which inclusions stick to the inner liner of the AG refractory.\(^{30}\)

Spoken roughly, there are two types of materials not prone to sticking. One is a carbon-free material\(^{31}\), since C and SiO\(_2\) do not coexist in it, they do not react with each other to form products in gas. Such a material is actually used at Yawata Works for the inner liner. The other is a material that forms a liquid phase on the inner nozzle surface, making it wettable with molten metal, so as to decrease the adhesive force of inclusions onto the nozzle surface. A refractory containing zirconia, lime stone, and carbon (called ZCG) is used for application at Kimitsu.\(^{31}\) A refractory consisting of dolomite and graphite (DG) and another consisting of dolomite\(^{32}\) have been proposed for the same use. The electromagnetic nozzle\(^{33}\) reported recently is another attempt to improve the wettability of the inner nozzle surface. Questions remain about the effectiveness of these refractories not prone to inclusion sticking: applicability to different steel grades and the durability of the effect. Considering the adverse effects of the sticking of inclusions over casting operation, further efforts will be made to devise other measures to prevent it.

(2) Measures against local corrosion\(^{34}\)

Casting powder, or mold flux, is used in the molds of continuous casters in order to protect molten steel against oxidation, catch inclusions, prevent the solidification shelf from sticking to the mold, and homogenize the heat transfer from the steel to the mold. The powder, however, corrodes the portions of submerged entry nozzles at the meniscus to determine the service life of the nozzles.\(^{35}\) For this reason, a zirconia-graphite (ZG) refractory, more resistant to corrosion than the AG refractory, is used for the nozzle portion contacting the powder (powder line). Improving the corrosion resistance of the ZG refractory is also effective at extending the service life of submerged entry nozzles.

It has been considered that, when the ZG refractory is in contact with the powder, ZrO\(_2\) grains in the aggregate are destabilized and disintegrate into smaller particles. This is a phenomenon peculiar to ZrO\(_2\) grains, and the fusion of the ZG refractory advances as the fine ZrO\(_2\) particles dissolve in the molten powder. Looking for measures to extend the service life of the ZG refractory in view of the above, effects of the grain size of ZrO\(_2\) aggregates\(^{36, 37}\), ZrO\(_2\) content in the refractory,\(^{38}\) chemical stability of ZrO\(_2\), purity of graphite,\(^{40}\) apparent porosity,\(^{41}\) etc., over the destabilization of ZrO\(_2\) and fining of its grains have been studied.

However, it is likely that the composition of the mold powder, especially its basicity, also exerts significant influence over the destabilization of ZrO\(_2\) and the fining of its grains.\(^{42}\) On the other hand, fine ZrO\(_2\) grains serve as a barrier at the powder-line surface to suppress the nozzle corrosion.\(^{43}\) Therefore, to further extend the service life of the ZG refractory, it will be important to investigate how it changes dynamically under the influence of the powder in consideration of the powder chemistry.

2.5 Repair and diagnosis technologies

Refractory repair work is done either online in hot or offline in cold. Hot repair is conducted by methods such as gunning, injection, filling and baking, and slag coating, and cold repair is conducted by methods such as gunning, patching, replacing, replenishing, and trowelling. Of these, remarkable advances have been made in the field of gunning. Nippon Steel Corporation has developed a variety of refractory gunning methods for stable operation of furnaces and vessels as well as for cutting refractory costs.

Dry gunning has been practiced since long; the method consists of conveying refractory powder to a blowing nozzle using air flow, mixing it with water at the nozzle tip, and projecting it to the refractory surface for repair. This method is simple, but the refractory layer thus formed is porous and lasts only a short period. As an improvement, wet gunning became popular in the late 1990s and thereafter. The shotcrete method,\(^{44}\) whereby premixed paste of refractory powder is pumped to a nozzle and gunned with compressed air, can form refractory layers denser than those by dry gunning, and is applied to the repair work of various furnaces and vessels. The rotary shot method,\(^{45}\) through which the refractory powder paste is projected centrifugally by a rotating machine, can handle refractory paste containing less water than that by shotcrete, and the deposited layer is yet denser. Another advantage of the rotary shot is that it can handle greater amount of refractory per unit time, and requires less labor.

The above wet gunning methods can deposit dense and durable refractory layers, but they are unsuitable for hot repair for fear of explosion of projected paste. Another disadvantage is that since the projected material is kneaded, the equipment has to be washed and cleaned after each use, which takes time and labor. Two hot gunning

![Fig. 4 Adhesion mechanism of alumina inclusions](image-url)
methods were developed to obtain durable refractory layers by simple operation: the “mist injection shot” method \(^{(46)}\)—whereby the refractory powder is conveyed to a blowing nozzle by air flow, mixed with water in the nozzle, and sprayed—and the “hot quick mixing injection & mist injection” (H-QMI) method \(^{(47)}\)—whereby the refractory powder is conveyed to a blowing nozzle using air flow and continuously mixed and gunned. The former is simpler to operate and applied to the repair of the well blocks of ladles and snorkels of degassers. The latter, on the other hand, is capable of forming more durable refractory layers and applied to converters and steel ladles.

Repair work is effective, efficient, and economical only when conducted on the basis of correct evaluation and diagnosis of refractory wear. Evaluation of refractory wear used to rely on human eyes, but use of profile meters enabled quantitative damage evaluation and effective repair. Laser profile meters made it possible to accurately detect local damage of ladle lining, etc., and hot gunning at the position extended the service life of the lining and reduced the amount of the refractory used. \(^{(48)}\) A combined system of damage diagnosis devices and flame gunning facilities capable of forming durable refractory layers was developed, applied to coke ovens, and proved effective at extending the oven life. \(^{(49)}\)

3. Closing

Steelmaking processes have changed continuously, and so have refractories to support the changes. The technologies of the material, structure, laying and application, diagnosis, and repair of refractory that compose the whole refractory technology must be further brushed up so as to help establish revolutionary steel producing processes. Refractories are also expected to continue to be instrumental in heat insulation for energy saving and cutting CO₂ emission, as well as recycling for resource conservation.

References

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