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Recent Advances in Refractories Technology for Steelmaking

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Abstract:

Refractories for holding molten steel occupy an important position among steelmaking facilities and have a very large impact on the manufacturing cost and quality of steel products. Increasing diversification and strictness of customer requirements in recent years have increased the severity of the steelmaking plant operating conditions for refractories. This report reviews changes made in major steelmaking processes in the past decade and the roles and issues of refractory engineers. It traces the development of long-life refractories and the automation of bricklaying work carried out to reduce refractories cost and improve steel quality. It lastly describes problems with refractories technology development to be solved in the future.

1. Introduction

Refractories for holding molten steel occupy an extremely important position among steelmaking facilities and have a crucial impact on the production cost and quality of steel products. The increasing severity of steelmaking plant operating conditions to meet the increasing diversification and sophistication of customer requirements in recent years have increased the harshness of service conditions for refractories. Refractory engineers have been endeavoring to reduce refractories cost and improve the steel quality by developing new refractories that have long service life and do not contaminate molten steel. Their targets of development include mechanization and automation technologies that reduce the bricklaying cost. This article reviews the advances made in Nippon Steel's steelmaking refractories technology in the past decade, and describes pending problems for the refractories engineers.

2. Past Changes in Steelmaking Process

The greatest consideration in the steelmaking process is stable production of high-quality steel at low cost. For this purpose, studies have been made continuously on the functional division of the steelmaking process and the realization of direct rolling. The division of steel refining functions made in the past is schematically illustrated in **Fig. 1**[1]. The refining functions were initially concentrated in the top-blowing converter. Now that the refining functions have been divided into three processes including the hot metal pretreatment and secondary refining processes, the present role of the converter is limited to decarburization. This development, on the other hand, has increased the diversity of steelmaking facilities and the severity of operating conditions in terms of molten steel temperature and molten steel keeping time, in order to ensure good matching between the interrelated facilities. This in turn has shortened the service life of refractories and created the new problem of molten steel contamination from refractories.

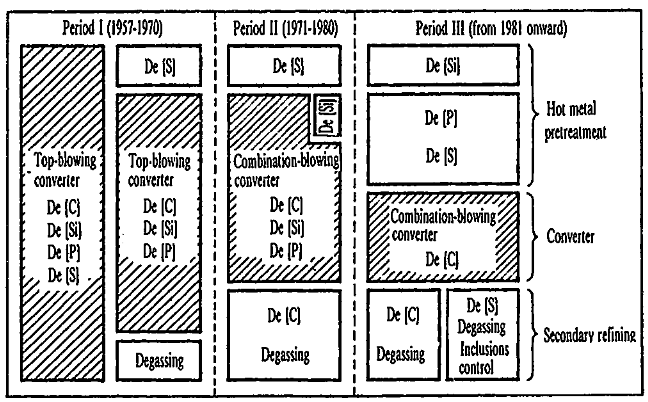

Fig. 1 Division of refining functions

In recent years, innovative processes, such as direct strip cast-

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ing and smelting reduction, have been developed for the purpose of drastically reducing steel cost through further process integration and streamlining. These newly emerging processes call for refractories with high-precision shapes and new functions.

3. Subject for Refractories Engineers and Development of Refractories Technology

Fig. 2 shows major steelmaking technology trends and major refractories issues, and development results in the past[2]. In recent years, the divided refining processes designed to achieve higher steel quality and productivity are gradually giving way to more innovative processes emphasizing high efficiency. Under these circumstances, refractories engineers have accomplished much in the development of durable refractories to meet the diversification of steelmaking furnaces, and in the establishment of optimum refractory lining structures and repair methods. In other words, the roles of refractories engineers in the steel industry are to advance the refractory material technology, optimize the refractories application technology, and combine these two technologies to realize innovative processes capable of manufacturing high-quality steel at low cost.

The roles of refractories engineers at Nippon Steel are schematically illustrated in **Fig. 3**. Development of refractories technology is led by Mechanical Technology & Refractory Development Center, Process Technology Research Laboratories and refractories technology groups at each works. It is also for the refractories engineers to propose optimum operating methods from the point of view of refractory properties to steelmaking divisions at the works and laboratories, and to show the basic policies of refractory material design to refractories manufacturers. The many development results noted above are an outcome of close cooperation among the steelmaking division, refractories manufacturer, and refractories engineers.

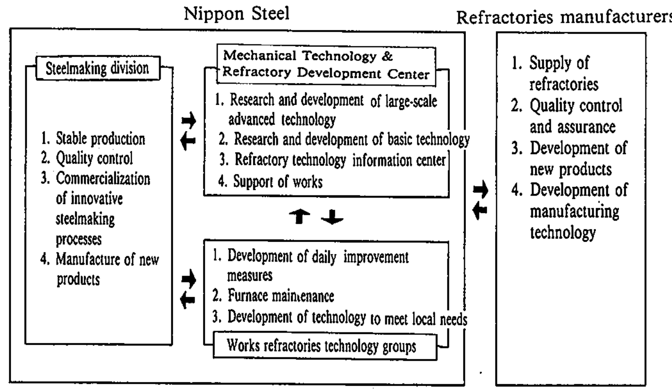


Fig. 3 Main roles of refractories engineers and their relations with steelmaking division and refractories manufacturers

As mentioned above, refractories technology has been innovated in various ways with the aim of raising the quality and lowering the production cost of steel products. Main approaches to these goals are described below.

3.1 Approach to cost reduction

To reduce the steel cost, the furnace life must be extended and the refractories consumption rate must be reduced. In 1982, Nippon Steel's refractories consumption was over 12 kg/ton-steel, but it fell to 9 kg/ton-steel or less in 1992, registering a drop of about 25% in a decade. The main factor in this success is the development of high-durability refractories to satisfy the properties required by specific furnaces. A typical example is the development of bricks with superior spalling resistance and slag penetration resistance using graphite, such as magnesia-carbon (MgO-C) brick and alumina-silicon carbide-carbon (Al_2O_3-SiC-

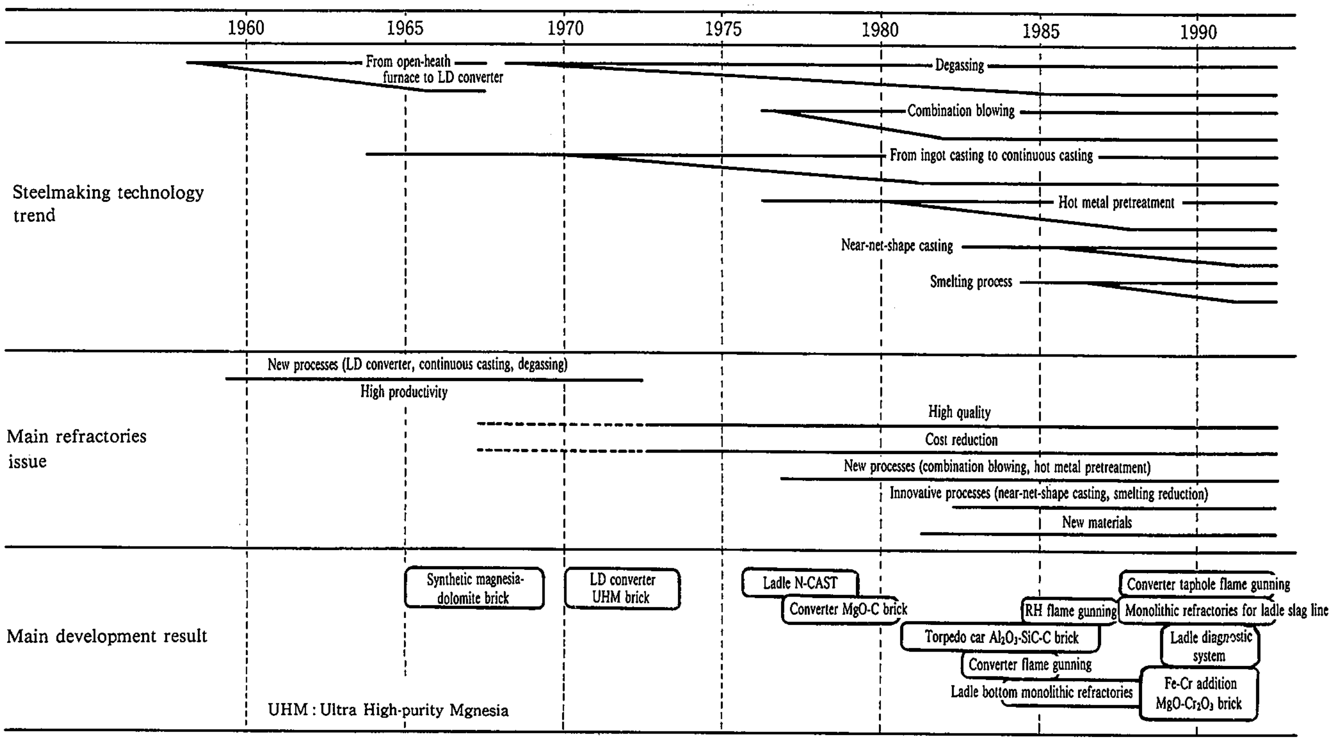


Fig. 2 Steelmaking technology trends and refractories issues; development results

C or ASC) brick. Development of magnesia-chromite brick with high purity and high density and hot repair technology for an abnormal wear zone should also be cited.

Reducing the brickwork cost by decreasing the furnace construction labor and increasing the bricklaying efficiency is an issue of equal importance. Nippon Steel is making positive use of monolithic refractories. Monolithic refractories already account for more than 65% of all the refractories used at Nippon Steel. This owes greatly to the development and extensive application of the method of building refractory walls by casting, called the N-CAST method[3]. Furnaces that must be constructed of brick because of the poor durability of currently available monolithic refractories require mechanization and automation of bricklaying work. In this connection, technologies have been developed to accurately diagnose conditions of refractory lining using various sensors and to repair furnaces by flame gunning.

3.2 Approach to steel quality improvement

The ever-growing call for higher steel quality makes it indispensable to use refractory materials that do not contaminate molten steel and are thermodynamically stable. For example, ladle refractories were formerly lined with acid refractories composed mainly of roseki or pyrophyllite. Today, they are lined with neutral refractories made of alumina and spinel. **Fig. 4** shows the internal defect incidence of steel handled in ladles lined with roseki brick or alumina spinel castable[4]. It is clear that nonmetallic inclusions do not readily arise from the alumina spinel castable that is stabler to steel. Recently, demand is mounting for basic castables, such as MgO and CaO, that are stabler than neutral castables.

There are some cases in which refractories themselves have no problem but are indirectly responsible for a steel quality problem. For example, the immersion nozzle used in the continuous casting process is liable to develop a problem of alumina deposition at its discharge hole, which is bound to affect the steel quality. This problem was solved by developing an immersion nozzle with the functions of not only corrosion resistance but also preventing the deposition of alumina near the discharge hole.

4. Progress of Refractories Technology for Steelmaking Facilities

4.1 Hot metal pretreatment

Introduction of hot metal pretreatment added the functions of reactor vessels to the conventional transportation functions of torpedo cars and hot metal ladles. Refractory linings of torpedo cars and hot metal ladles greatly changed with the change of their service conditions. **Fig. 5** shows changes in the hot metal pretreatment process and refractories consumption rates[5]. Torpedo cars and hot metal ladles were formerly lined with chamotte brick and high-alumina brick. When hot metal pretreatment started to be pretreated in torpedo cars in or around 1982, refractories wear increased and the refractories consumption rate rose to 1.5 kg/ton-pig iron. This high refractories consumption gradually declined as a result of the development of ASC brick and glass-addition ASC brick.

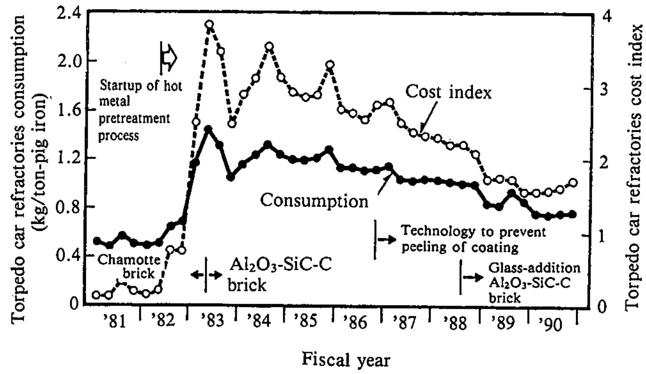


Fig. 5 Changes in torpedo car refractories consumption and refractories cost index

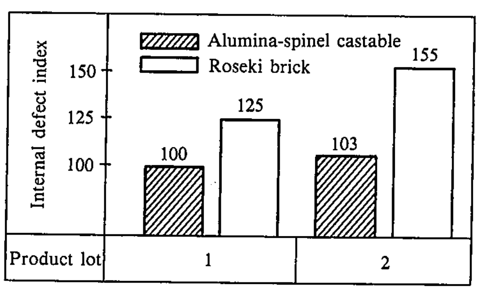


Fig. 4 Internal defect index of steel handled in ladles with bottom constructed of pyrophyllite brick and alumina spinel castable refractories

ASC brick combines the corrosion resistance of alumina with the spalling resistance and slag penetration resistance of graphite, and contains silicon carbide (SiC) to prevent the oxidation of graphite. The in-service oxidation of graphite and SiC has a great impact on the durability of ASC brick. High-durability ASC brick was developed by preventing the oxidation of graphite by adding metals, such as aluminum and silicon, or glasses, such as borosilicate glass and phosphate glass[6,7].

ASC brick, however, has so high thermal conductivity as to bring about the problems of hot metal temperature drop and shell deformation during transportation. These problems have been solved by reducing graphite and SiC[8] and installing insulating boards to ASC brick-lined torpedo cars[9].

4.2 Converters

When introduced into Japan in the 1960s, converters were lined with tar-dolomite brick and stabilized burnt dolomite brick. The refractories were then replaced by semistabilized burnt dolomite brick and tar-bonded and fired brick made of synthetic magnesia-dolomite clinker. High-purity burnt magnesia brick was also used in some converter linings. In the late 1970s, magnesia-carbon (MgO-C) brick with corrosion and spalling resistance was developed and rapidly brought into common use. It utilizes the resistance of magnesia (MgO) to the corrosive high-basicity slag and the high thermal conductivity and low slag wettability of graphite. Today, magnesia-carbon brick accounts for more than 95% of the converter lining brick.

The durability of magnesia-carbon brick can be increased by preventing the oxidation of graphite and improving the corrosion resistance of magnesia clinker. The former requirement has been effectively met by adding such easy-to-oxidize metals as aluminum and magnesium-aluminum, carbides such as silicon carbide (SiC)[10] and boron carbide (B_4C)[11] and borides such as calcium boride (CaB_6)[12], and by applying high-purity graphite (see **Fig. 6**)[11]. The latter requirement has been met by raising the purity of magnesia clinker[13], using electrofused magnecia (see **Fig. 7**) and optimizing particle size distribution of magnesia

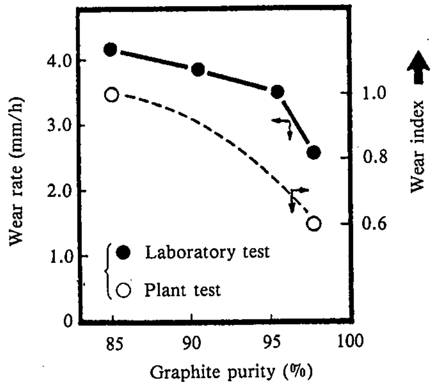


Fig. 6 Effect of graphite purity on wear rate of magnesia-carbon brick

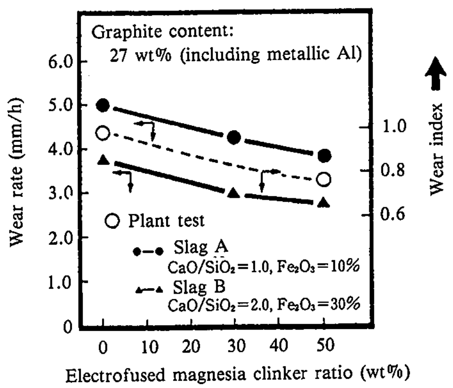


Fig. 7 Effect of electrofused magnesia ratio on wear rate of magnesia-carbon brick

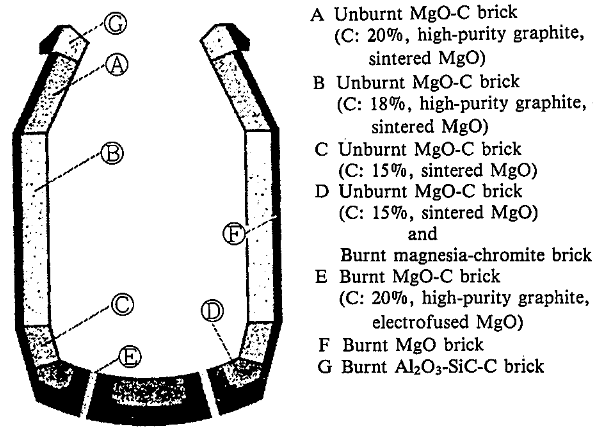


Fig. 8 Example of zoned lining of combination-blowing converter

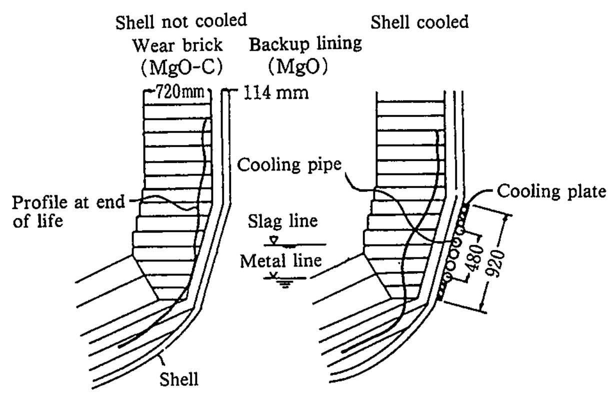


Fig. 9 Comparison of wear with and without shell cooling

clinker[11].

Magnesia-carbon (Mg-C) brick to which zircon ($ZrSiO_4$) is added for thermal stress alleviation in service was also developed[14]. In the converter lining, different factors are responsible for the wear of different parts. Therefore, the zoned lining method whereby different types of magnesia-carbon brick are installed in different lining areas to assure wear balance, as shown in **Fig .8**, is extremely important in extending the converter life and reducing the refractories cost.

Many studies have been made on the converter operation and equipment. Study themes include the slag coating practice whereby the refractory lining surface is coated with slag; a slag control method whereby a magnesia source such as soft-burnt dolomite is added to the slag to inhibit the dissolution of refractories components into the slag; and a cooling method whereby the vessel is cooled to control slag deposition and inhibit refractories wear, as shown in **Fig. 9**[15]. The converter campaign life was gradually extended by these equipment measures and operational measures combined. Nagoya recorded a converter life of 6,301 heats with a refractories consumption rate of 0.46 kg/ton-steel[16].

4.3 Secondary refining process

Nippon Steel operates many types of secondary refining units, including RH, DH, LF, VOD, and V-KIP. The RH process has a particularly serious problem with refractories. High-alumina brick was initially used when the process was introduced. Today, magnesia-chromite basic brick with high corrosion resistance is used to accommodate the extended treatment time and increasingly severer service conditions exemplified by flux addition.

Generally, magnesia-chromite brick cannot have both spalling resistance and corrosion resistance at the same time. These two properties are closely related to the amount of chromite mixed in the brick[17]. Chromite invariably contains such impurities as SiO_2, Al_2O_3 and Fe_2O_3. SiO_2, in particular, is a major factor in the decrease of corrosion resistance in magnesia-chromite brick, as shown in **Fig. 10**[18]. High-purity clinker with a reduced SiO_2 content is used for higher durability[19].

Magnesia-chromite brick with added Fe-Cr metal powder was developed to obtain still higher corrosion resistance[20]. Pores in the brick are filled by the volume expansion caused by the Fe-Cr oxidation and spinel formation during the firing of the brick. The brick is thus densified to last longer in service. **Fig. 11** shows the effect of Fe-Cr addition on the corrosion resistance and slag penetration resistance of magnesia-chromite brick. The Fe-Cr metal powder proves effective when its addition exceeds 3%. Magnesia-chromite brick of this type is already commercialized[21].

4.4 Ladles

Roseki brick was traditionally used as a popular ladle lining material. Roseki brick forms a viscous liquid film on the hot face so that slag and metal penetration and buildup are small. Increased secondary refining ratio has raised molten steel temperature and prolonged molten steel residence time, which in turn

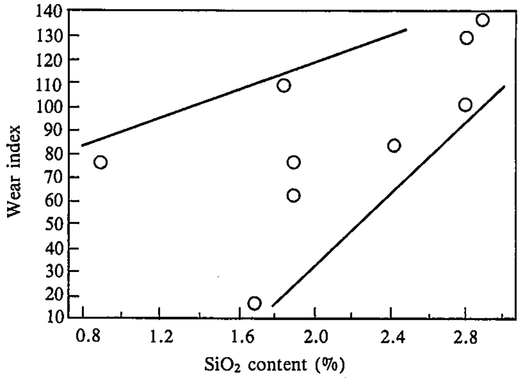


Fig. 10 Effect of SiO_2 content on wear index of magnesia-chromite brick

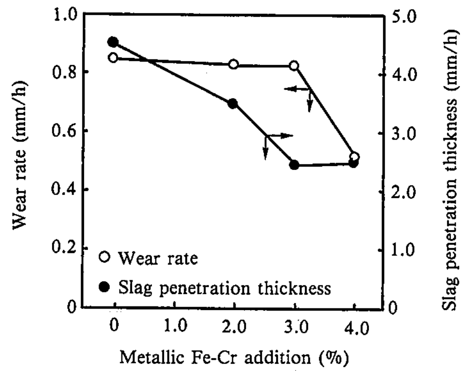


Fig. 11 Effect of Fe-Cr addition on wear rate and slag penetration thickness of magnesia-chromite brick

has increased the wear rate and lowered the steel quality. Reduction in refractories installation labor has increased demand for the use of monolithic refractories to line ladles. Ladle sidewalls were formerly lined with silica and roseki zircon-based castables and are now lined with alumina-spinel castable refractories[22]. Problems with a monolithic refractory bottom are convex deformation under thermal stress in operation and steam explosion during drying. The former problem was solved by adding stainless steel wire, and the latter by adding organic fiber to provide permeable pores[4].

Castable refractories are being applied also to the slag line. Krosaki, Harima Ceramic, and Nippon Steel jointly developed a new "magnesia-zirconia clinker" combining the resistance of magnesia to corrosion by high-basicity slag with the slag penetration resistance of zircon. The magnesia-zirconia castable has allowed ladles to be entirely lined with monolithic refractories as shown in **Fig. 12**[23].

4.5 Continuous casting

The continuous casting process decides the ultimate quality of steel, and therefore uses refractories with many specialized functions.

Tundishes were traditionally lined with roseki chamotte brick but now are lined with high-alumina castables for labor and cost savings. The tundish inside wall is normally troweled or sprayed with a magnesia-based coating material to improve the quality of cast steel, simplify the deskulling work after casting, and protect the tundish base material.

The immersion nozzle used to pour molten steel from the tundish into the mold was initially made of fused silica to secure thermal shock resistance and corrosion resistance combined. Continuous casting of high-manganese steel gave an impetus to the use of alumina-graphite (Al_2O_3-C) immersion nozzles. Alumina graphite is a mixture of alumina having high thermal stability and high steel corrosion resistance with graphite having high thermal shock resistance. Metals and carbides are added in trace amounts to improve oxidation resistance. Alumina graphite nozzles clearly show powder line wear as the casting time extends. For this reason, zirconia graphite (ZrO_2-C) is used at the powder line, and is cast integral with alumina graphite. When the immersion nozzle is used for casting low-carbon aluminum-killed steel over a long period of time, alumina builds up near the outlets, as shown in **Fig. 13**, changes the discharge stream direction, and creates a serious steel quality problem. The alumina buildup often makes it impossible to secure the desired pouring rate, resulting in an abort in an extreme case. There are many reports discussing about the causes of the alumina buildup[24]. The deposition of alumina clusters from the steel is the largest factor. Valid solutions to this problem include: injecting argon into the noz-

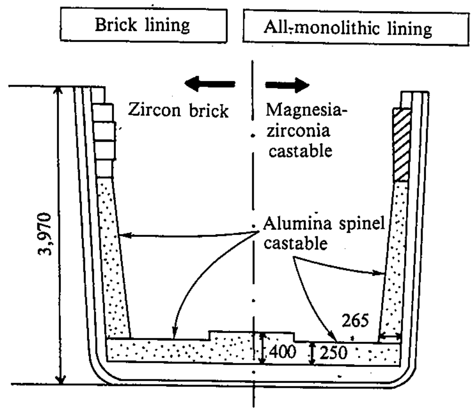


Fig. 12 Schematic illustration of all-monolithic ladle lining

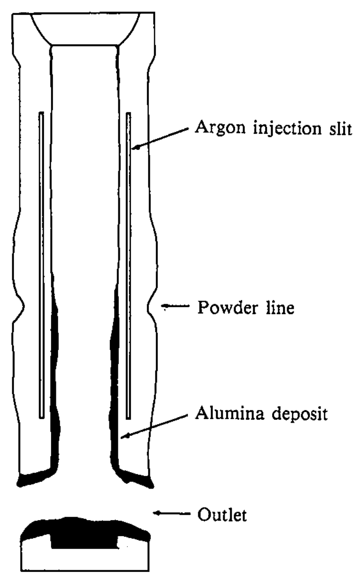


Fig. 13 Schematic illustration of alumina deposit on immersion nozzle

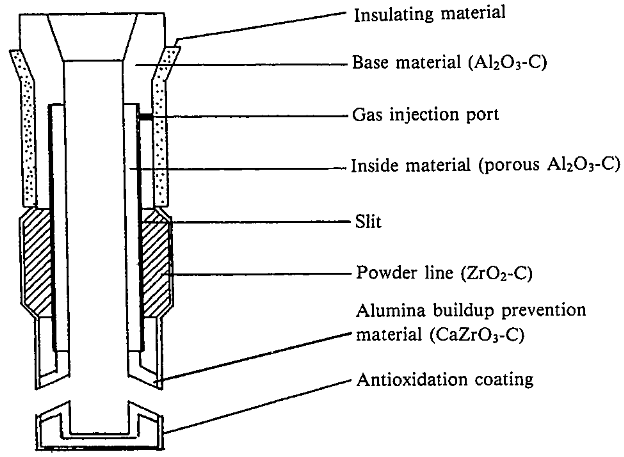


Fig. 14 Schematic illustration of immersion nozzle protected against alumina buildup

zle bore as shown in **Fig. 14**; a nozzle lined with a calcium zirconate-graphite ($CaZrO_3$-C) material that forms a low-melting point compound with alumina[25]; and a nozzle with improved bore surface roughness[26].

5. Installation, Diagnosis, and Repair

The largest problems with the use of monolithic refractories are long drying time and steam explosion. These problems are successfully coped with by developing a drying unit that uses microwaves and hot air in combination, and commercializing a short-time and steam explosion-free drying technique[27]. For converters mainly lined with brick, the block method[28] using a brick lifter and a bricklaying robot[29] is employed to save bricklaying labor and time.

Control of furnaces in operation requires the accurate measurement of the lining thickness and monitoring of furnace conditions. Technology of measuring the lining thickness and detecting metal penetration by a ladle lining diagonostic system using eddy current, as shown in **Fig. 15**[30]; technology of detecting brick cracks by elastic shock waves[31]; and and ITV furnace condition monitoring system[32] are in commercial application.

Adequate repair of abnormal wear areas is extremely important in extending the furnace life. These wear areas were formerly repaired by patching, or by personnel who entered the furnace after it was cooled down. Today, such repair work is done quickly in the hot condition by machines. **Fig. 16** shows a flame gunning repair unit for converters[33]. The fine refractory particles are melted in propane and oxygen flame and sprayed onto the repair area and forms an extremely durable body on the surface to be repaired. Given its high effectiveness, the flame gunning repair unit is also applied to RH vacuum degassers and ladles, among other things. Converter linings were traditionally repaired by gunning as visually observed by workers. Now, the relationship between the wall temperature and the optimum moisture content of repair material is quantified beforehand, and accordingly the repair material is automatically spray gunned to make a long-lasting body efficiently[34]. For RH lower vessels and snorkels, a non-water-based grouting material is used for quick repair with relatively small thermal shock to the base material[35].

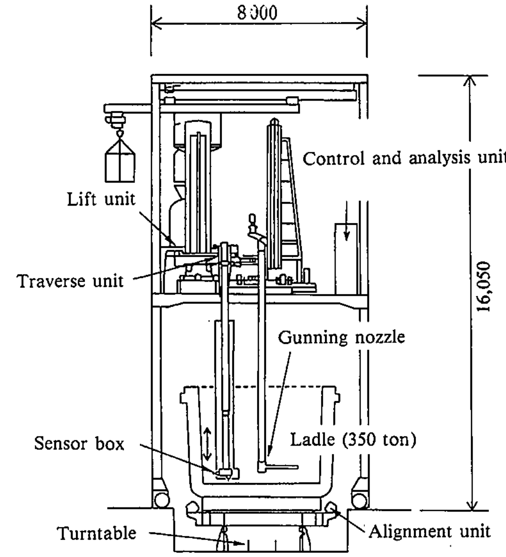
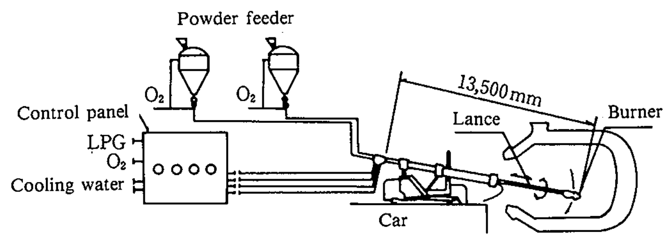


Fig. 15 Schematic illustration of ladle lining diagnosis system



LPG	200 Nm^3/h (at 1 kg/cm^2G)
O_2	1,000 Nm^3/h (at 5 kg/cm^2G)
Cooling water	30 Nm^3/h
Capacity	1.5 - 2.0 t/h

Fig. 16 Outline of flame gunning repair system

6. Future Issues of Refractories Technology Development

Steelmaking processes will continue to be simplified and integrated to a greater extent than ever for the purpose of cost reduction. Researches are under way to develop truly innovative processes. Refractories hold the key to the success of such efforts. For example, durability of refractories for pouring nozzles and side dams determines the success or failure of strip casting, and also has important bearings on the strip production cost, productivity and quality. All this indicates the importance of developing novel refractory materials and structures along with the progress of steelmaking processes.

The technology of mass melting steel scrap in the converter now under development makes it urgently necessary to develop superhigh-temperature refractories that can accommodate the high furnace temperature expected from the increasing amount of post combustion. A new technology will have to be developed to fulfill this purpose. It is also important to introduce new technology such as superfine powder processing technology cultivated in the field of advanced ceramics, and refractories cooling technology.

The furnace refractories maintenance also poses many problems. Considering the scarcity of young personnel fit for work in dirty, demanding, and dangerous environments and the aging of skilled workers, it is imperative to use more monolithic refractories in steelmaking and refining furnaces, to automate bricklaying, and to make refractories repair equipment intelligent enough to take the place of skilled workers. These and many other problems call on refractories engineers to further intensify their research and development efforts.

7. Conclusions

Refractories technology is an indispensable element of the steelmaking technology. It has played major roles in the past, and now, it is faced with many critical problems. Refractories engineers ought to deepen their coordination with steel engineers and other operating personnel as well as refractories manufacturers in their endeavor for further developing refractories technology, so that steel products of better quality and lower cost can be offered to the increasingly discriminative customers.

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