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Technical Report

Technical Development of Refractories for Steelmaking Processes

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Abstract

Refractory technology for steelmaking has developed significantly over the last 25 years in response to changes in the steelmaking processes and increasingly strict requirements for better corporate performance. Principal process changes include the introduction of new process steps such as hot metal pretreatment and ladle refining and an increase in the continuous casting ratio. Against these backgrounds, the development of refractory technology for steelmaking processes is explained using examples at the Kimitsu and Muroran Works.

1. Introduction

Steelmaking processes have changed remarkably over the last 25 years. For example, the functions of refining from iron to steel have been divided into various processing stages, such as molten iron pretreatment and secondary refining, and the continuous casting ratio has increased dramatically. In the meantime, the need for higher productivity, quality improvements and cost reductions became increasingly severe. In response, technology concerning refractories, which make direct contact with the molten pig iron and steel during these various processing stages, has shown remarkable progress. This paper explains the technical development of refractories for steelmaking processes focusing on typical examples at the Kimitsu and Muroran Works of Nippon Steel Corporation.

2. Technical Development of Refractories for Reactors and Vessels for Steelmaking

2.1 Torpedo Cars[1)]

Fig. 1 shows the inner lining of a torpedo ladle car, and **Fig. 2** schematically illustrates the work methods for relining and repairing the torpedo car's lining. The worn and permanent bricks are replaced with new ones during each large periodical repair, and thereafter, intermediate repairs are done once every 100 to 160 heats. The tasks during intermediate repairs are remolding of the unshaped refractory at the mouth, replacement of damaged bricks with new ones and padding of worn lining with unshaped refractory. Large periodical repairs are done after 10 to 25 intermediate repairs.

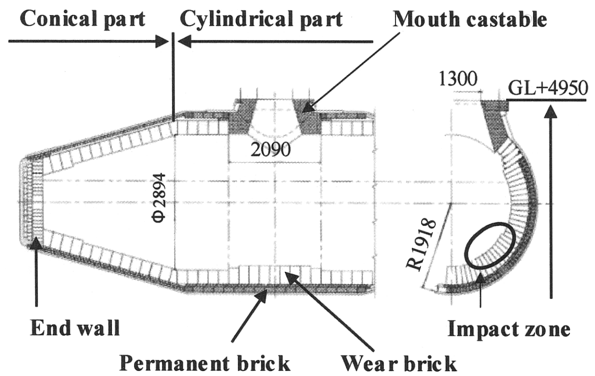

Fig. 1 Lining of torpedo car

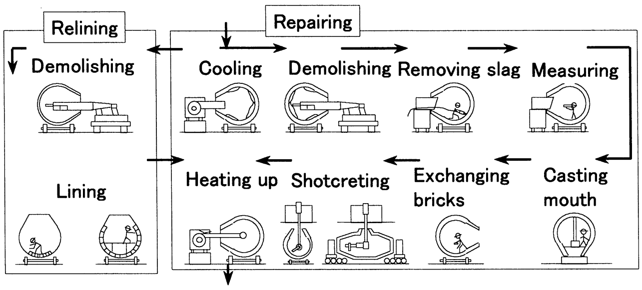

Fig. 2 Item of repairing and relining on using shotcreting

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Fig. 3 shows outlines of two routes for the optimum refining processes (ORP) of hot metal employed at Kimitsu Works. The upper (old) route, called the torpedo-type ORP, was in operation from 1983 to 1999, whereby molten metal first underwent desiliconization with the addition of FeO at the pig iron runner in the blast furnace cast house; then in a torpedo car, it was dephosphorized and desulfurized by bubbling a flux of CaO, etc. with oxygen, and finally decarburization took place in the converter. The old route was replace by the one shown in the lower part of Fig. 3 (herein called the converter-type ORP) in 1999, whereby no treatment is undertaken in the torpedo car, and the hot metal first undergoes desulfurization by the KR process in a hot metal ladle before being charged into the converter, wherein dephosphorization, desiliconization and decarburization proceed.

Before the introduction of the torpedo-type ORP in 1983, high-grade chamotte brick was used to line the torpedo cars. However, because of the FeO addition and hot metal treatment in the car, FeO and CaO content in the slag increased, causing the slag to react with SiO_2 and Al_2O_3 in the chamotte brick to form low-melting-point products such as $2FeO \cdot SiO_2$ (fayalite, melting point: 1,210℃), $FeO \cdot Al_2O_3$ (hercynite, melting point: 1,450℃), and $CaO \cdot Al_2O_3 \cdot 2SiO_2$ (anorthite, melting point: 1,550℃). Consequently, the intervals between large periodical repairs of torpedo cars decreased to about a half that before the introduction of the torpedo-type ORP.

As a countermeasure, a new type of brick based on an Al_2O_3-SiC-C system was developed by increasing the Al_2O_3 content to improve corrosion resistance, and adding carbon to improve resistance to spalling and slag infiltration and SiC to prevent the oxidation of carbon. Thereafter, various improvement measures have been applied to the Al_2O_3-SiC-C brick to prevent damage to brick joints and wear by flaking. One such measure is the Al_2O_3-SiC-C + glass brick with the addition of metallic Al and glass that Shimada et al. reported,[2] and another is the Al_2O_3-SiC-C + MgO brick with the addition of MgO to take advantage of the swelling of $Al_2O_3 \cdot MgO$ that Kataoka reported.[3-5] **Table 1** lists the types of bricks developed and used for torpedo cars.

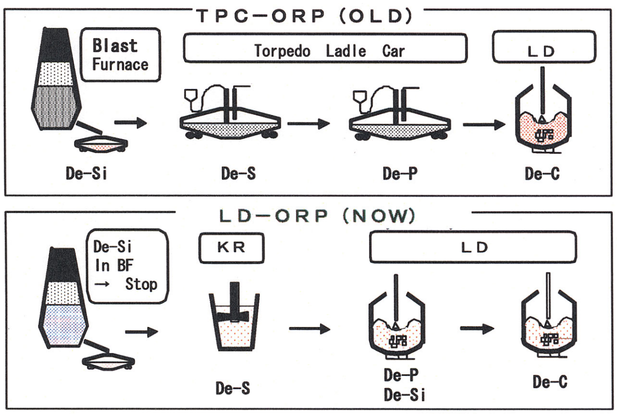

Fig. 3 Pretreatment of hot metal

Worn torpedo car lining bricks were initially repaired during intermediate repairs by spraying on an Al_2O_3-SiO_2 material. Afterwards, to accelerate the deaeration of the coating material by applying vibrations to improve its durability, the vibro-trowel coating method was introduced. However, because the method required hours of muscular labor by many workers and the adhesion of the coating material was not as good as expected, it was later replaced by a new wet spraying method called the “shotcreting” method, which will be explained in more detail in Subsection 2.4. At that stage, to save labor and protect workers from the strongly alkaline quick-setting admixture used for the coating work, an automatic shotcreting station was designed and constructed (see **Fig. 4**)[6, 7]. In consideration of structural stability and resistance to corrosion and wear, etc., an Al_2O_3-SiC-C system, the same material as that of the wear bricks, was selected as the main constituent of the coating material. The new torpedo car repair station was commissioned in 1999.

At the same time, bearing in mind the importance of knowing the remaining lining thickness, a lining thickness measuring system using two-dimensional thermometers was constructed.[1] **Fig. 5** shows the outlines of the system. Automatic two-dimensional thermometers provided along the hot metal transport route measure the whole temperature profile of each loaded torpedo car every time it passes their locations, and the wear of the lining is estimated based on the temperature information and the number of heats since the last repair.

As a result of these measures, the lining life began to increase. Then, the converter-type ORP was introduced in 1999, and after the roles of torpedo cars as reaction vessels for dephosphorization and desulfurization were eliminated, they became simple containers for hot metal transport. Because the addition of flux such as FeO and CaO, which was detrimental to the lining life, was discontinued, the wear on bricks at the slag line and impact zone decreased significantly. Consequently, the interval between the large and intermedi-

Table 1 Type of bricks

		Chamotte	Al_2O_3-SiC-C	Al_2O_3-SiC-C + glass	Al_2O_3-SiC-C + MgO
Period of use		-1983	1982-89	1986-94	1994-
Al_2O_3	(%)	43	50	70	64
SiO_2	(%)	51	17	3	3
SiC	(%)		19	10	10
F.C	(%)		12	15	14
MgO	(%)				8
Glass				○	○
Apparent porosity	(%)	12.4	10.9	4.8	5.0
Bulk density		2.3	2.9	3.1	3.1
Crushing strength	(MPa)	106	38	52	51

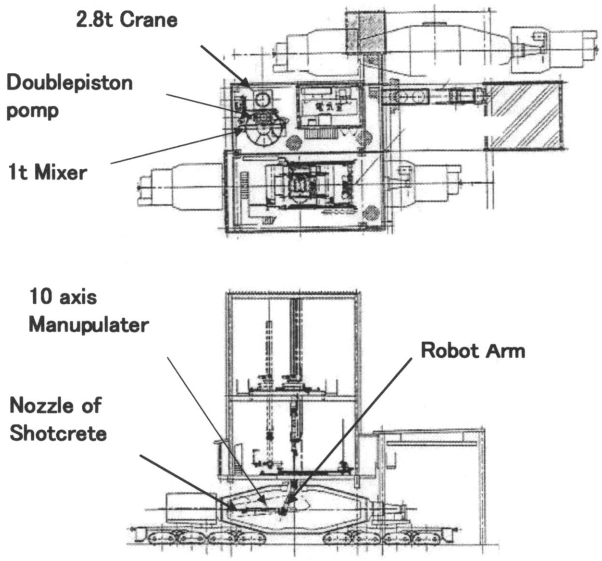

Fig. 4 Automatic shotcreting apparatus

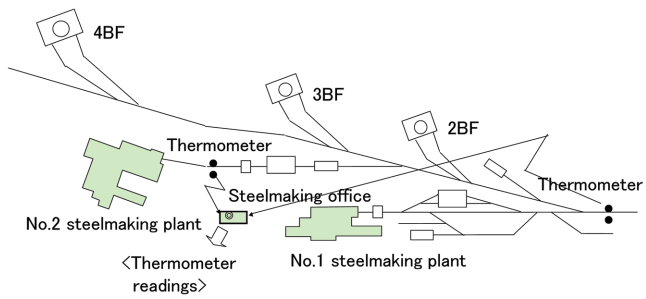

Fig. 5 Measuring system of shell temperature using 2-dimensional thermometers

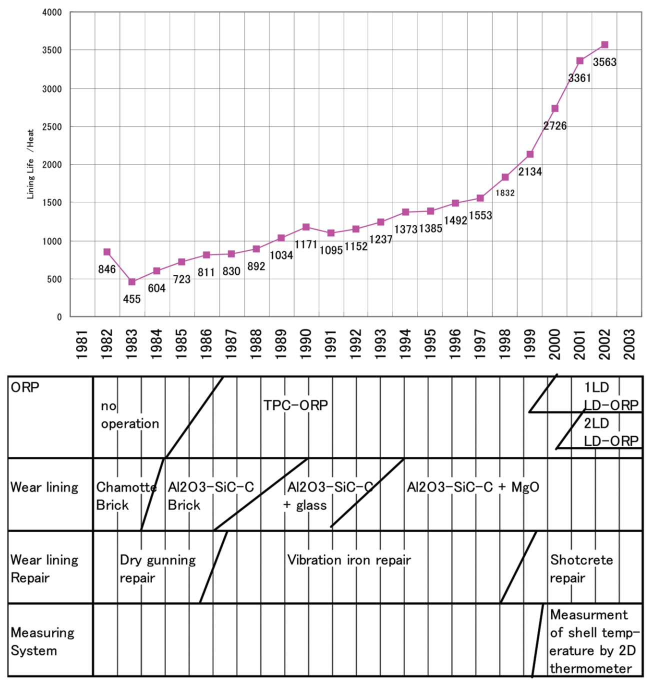

Fig. 6 Change of operation, lining and repair and trend of lining life

ate repairs became much longer than those even before the torpedo-type ORP, and the net working rate of torpedo cars increased by 20%, coping well with production needs, which had increased by 40% in the meantime. As a result, the unit costs for refractory and repair work on torpedo cars decreased remarkably. **Fig. 6** shows the correlation between the lining life of torpedo cars between large repairs, the change in the ORP methods and the time sequence of the new technologies described above.[1)]

2.2 Converters

2.2.1 Brick-Fixing Structure in Conical Portion[8)]

At the Kimitsu and Muroran Works, the lining life of converters was determined at one time not by the refractory erosion at the bottom and cylindrical portions but by the falling of bricks in the conical portion. The countermeasures taken at No. 2 Steelmaking Plant of Kimitsu Works are explained below.

In the first place, to prevent bricks from falling, they were secured to the steel shell using metal fittings as shown in **Fig. 7**; each brick was fixed to the shell by a hooked metal fitting engaged with a slit in it at one end and welded to the shell at the other. Here, the brick was wrapped with a metal case as seen in **Fig. 8** so that the cases fused to each other to prevent the bricks from falling. However, since these measures could not totally prevent the falling of bricks, additional measures were taken: a non-slip coating was applied to the brick surfaces, and a small amount of powder pitch was added to the brick material to improve resistance to heat spalling. In addition, in consideration of deformation of the furnace shell due to causes such as thermal loads, special attention was paid to the brick-laying work to select a brick having exactly the correct taper for

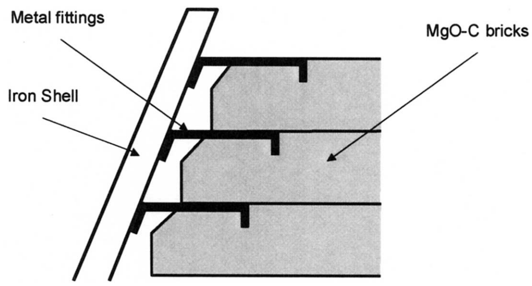

Fig. 7 Brick-fixing structure in the cone of BOF

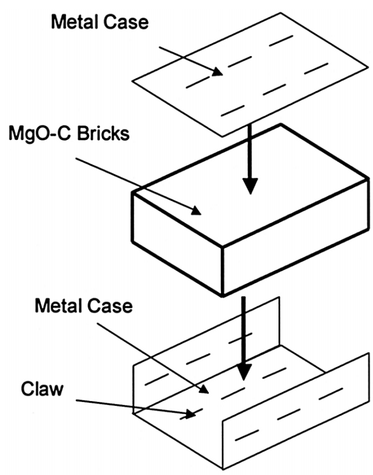

Fig. 8 MgO-C brick with metal case

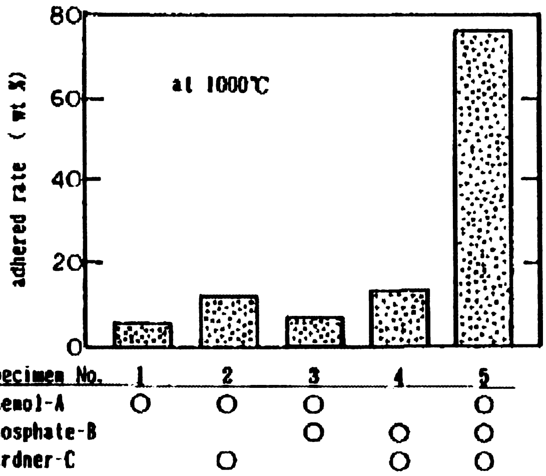

Fig. 9 Relation between combination of binders and adhered rate

each position so as not to cause the joints to separate at the back. The falling of bricks has been effectively prevented by this combination of measures.

2.2.2 Resin Materials for Spraying[9)]

Measures to extend the life of MgO-C bricks for converter lining include slag coating whereby the slag is made to stick to the surface of the lining, and slag control whereby the concentration of MgO in slag is adequately controlled to suppress the elution of refractory constituents to the slag. When damaged, the lining is repaired by flame-spraying or dry-gunning of unshaped refractory materials. A gunning material composed of MgO aggregate and phosphate binder was widely used in the 1980s.

In order to improve the life of lining formed by gunning, Muroran Woks developed a new gunning material by changing the grain size distribution of magnesia clinker (35% larger than 1 mm, 35% smaller than 0.125 mm) and using the same powder phenolic resin, phosphate and hardener as those for MgO-C brick. **Fig. 9** shows the results of adhesion tests by gunning specimens containing different binders onto a vertical wall. It is clear from the graph that the combination of the three binders (Specimen 5) led to a significantly better adhesion rate. The developed gunning material was commercially introduced at Muroran and showed excellent adhesion and durability, whereupon its use expanded to other Works at Nippon Steel and also outside the company.

2.3 Secondary Refining

In order to eliminate the use of refractory containing chromium, Kimitsu Works is promoting the use of unshaped refractory for vessels for RH degassing.

2.3.1 Lower RH Vessel[10)]

For the first time in the world, Nippon Steel began to use unshaped refractory for the lower RH vessel at Oita Works in 1996; a microwave hot air dryer was used to dry the refractory.[11)] However, the drying time was initially as long as 110 hours. The authors studied the introduction of a microwave dryer at Kimitsu Works for the same purpose, but it was necessary to realize a longer lining life through a shorter drying time.

As a measure to extend the lining life, organic fiber, which had been mixed with the lining material to prevent explosion during drying, was eliminated. As a result, the porosity of the test specimens decreased by about 1%, and the bending strength increased by about 10%.

Next, the following modifications were introduced to the microwave dryer: (1) installation of reflector plates to hide microwave-absorbing objects other than the applied unshaped refractory; (2) modification of stirrers such that the microwave is irradiated evenly to all the surface of the refractory; and (3) positional change of the hot blast tube to minimize the temperature difference of the refractory in the thickness direction.

A new heating pattern was developed for the drying in consideration of the following points: (1) rapid heating up to the temperature range devoid of the danger of explosion in such a manner that the energy input in the form of microwave and hot air is used to heat the refractory mixture as efficiently as possible; and (2) use of the energy input not for heating the refractory proper but for the evaporation and removal of water from the mixture.

Fig. 10 shows the positions of the thermometers, and **Fig. 11** an example of temperature measurement results. Thanks to the above measures, it became possible to shorten the drying time to 83 hours. The microwave drying process was introduced to Kimitsu Works, and the lining life increased from 260 to 350 heats while refractory costs decreased by about 30%.

2.3.2 Upper RH Vessel[12, 13)]

Conventionally, $MgO-Cr_2O_3$ (magnesia-chromite) bricks were used for the upper RH vessel. The principal factors behind damage to the refractory of the vessel included (1) fusing by FeO due to melting and flowing of steel skulls on the refractory surface, (2) cracking and falling at the joint between the upper and lower vessels on the occasions of the change of the lower vessel, and (3) cracking and flaking due to heating and cooling. For unshaped refractory to be

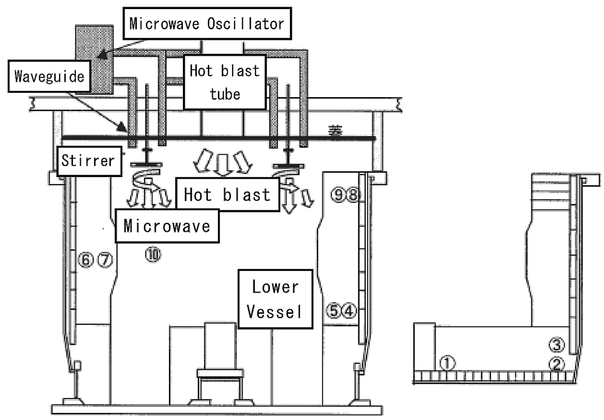

Fig. 10 Temperature measuring points in the lower vessel

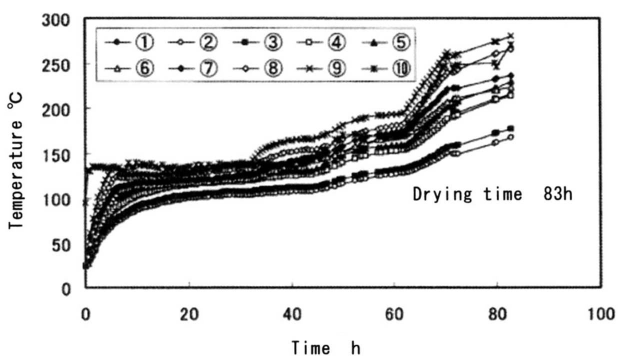

Fig. 11 Temperature change in the lower vessel by new drying patern

usable for the upper RH vessel, it was necessary to have the same or better material strength, FeO fusing resistance and spalling resistance as those of the magnesia-chromite brick.

In consideration of the above, the authors compared magnesia-chromite brick and alumina-spinel castable refractory in terms of FeO fusing resistance using the rotating erosion test. Ordinary carbon steel was used as the eroding material, and the test temperature and time were set at 1,600°C for 6 hours. **Fig. 12** shows the results; the alumina-spinel castable refractory exhibited erosion resistance superior to that of the magnesia-chromite brick. Heat-spalling resistance was evaluated by heating specimens in common brick shapes to 1,400°C and then cooling to room temperature; the alumina-spinel refractory proved to be equivalent to the magnesia-chromite brick.

Based on the above results, cast forming of the alumina-spinel refractory was selected for the lower wall and joint of the upper RH vessel. As for the upper wall, since the refractory lining of this portion is only slightly damaged, alumina-magnesia unshaped refractory was selected for application using the shotcrete method, a simpler method of refractory application. **Table 2** shows the types of refractories used for the upper RH vessel.

The selected refractory materials perform satisfactorily without abnormal erosion.

2.4 Repairs[14)]

For the refractory lining of various types of vessels, use of unshaped materials combined principally with cast forming was widely promoted. Casting, however, requires molds and takes a long time for their assembly and disassembly as well as for hardening and curing of the cast material. As an improvement measure, the wider application of wet-mixed shotcreting was studied.

Fig. 13 schematically shows the equipment configuration for the shotcreting method. Unshaped refractory material in a slurry coming from the mixer is pumped by a piston-type or squeeze-type pump to the nozzle, where it is mixed with a hardening agent and sprayed by compressed air onto the surface to be protected by forming a refractory layer. **Fig. 14** shows the relationship between the feeding rate and the porosity of the layer formed by different working methods. It is clear from the graph that the shotcreting method has a feed-

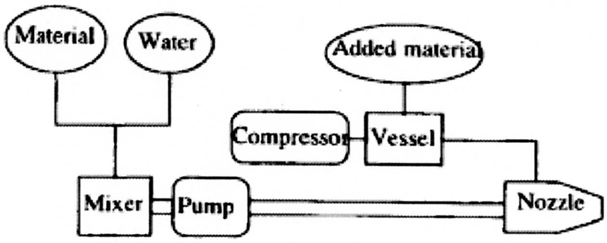

Fig. 13 Outline of shotcreting system

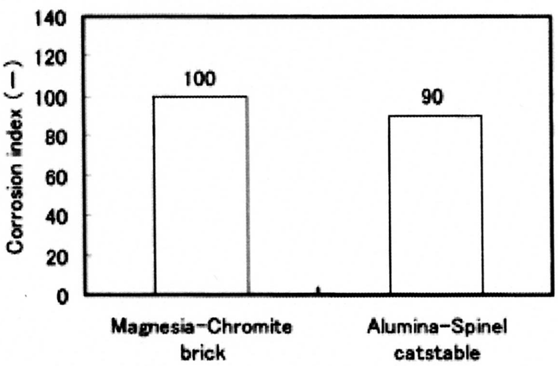

Fig. 12 Results of corrosion test by iron oxide

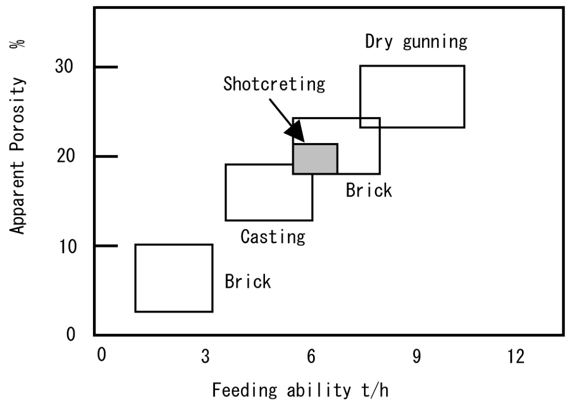

Fig. 14 Comparison of construction methods

Table 2 Unshaped refractories for upper vessel

		Conventional	Improvement	
Section		Wall	Lower wall	Upper wall
Material		Magnesia-chromite brick	Alumina-spinel castable	Alumina-Magnesia shotcrete
Properties				
Bulk density		3.05	3.14	2.9
Apparent porosity (%)		16.5	16.5	21.0
Modulus of rupture (MPa)	Room temperature	5.9	4.5	3.1
	After heating to 1,500°C	3.9	22	-
Chemical composition (%)				
Al_2O_3		-	91.8	89
MgO		72.5	6.8	7
Cr_2O_3		12.2	-	-

Table 3 Outlines of shotcreting vehicle

Name	Mobile-shot
Vehicle	Truck (8ton)
Material pump	Piston pump
	100 kg/min
Mixer capacity	500 kg/batch
Air compressor	11 m^3/min

Table 4 Typical properties of ladle lining materials

		Conventional	Improve	Castable
Chemical composition				
(%)	Al_2O_3	88	86	89
	MgO	10	12	7.5
Modulus of rupture				
(MPa)	110℃× 24h	11.2	10.3	7.0
	1,500℃× 3h	29.7	27.1	31.1
Permanent linear change		+0.02	+0.83	+0.83
(%)	1,500℃× 3h			

ing rate nearly as high as that of the dry-gunning method and is capable of realizing a porosity close to that obtainable by casting.

In introducing the shotcreting method for different applications, aiming for versatility and a high operating ratio, a whole set of shotcrete equipment was designed on a vehicle-mounted system. Its outline specifications are presented in **Table 3**.

Test applications to torpedo ladle cars and molten steel ladles were conducted using the vehicle-mounted equipment. Here, an unshaped material of the same constituents as those of Al_2O_3-SiC-C brick for torpedo cars was sprayed on occasions of their intermediate repair after approximately 450 heats. The shotcreted layer withstood more than 120 heats, and substrate bricks were found to have undergone little wear. In appreciation of this, the automatic shotcreting station shown in Fig. 4 was constructed exclusively for the repair of torpedo cars.[1)]

The lining structure selected for molten steel ladles was that of an alumina-magnesia unshaped material applied by shotcreting onto an alumina-magnesia layer formed by casting.[15)] To suppress flaking due to shrinkage during protracted use at high temperatures, fine alumina more than 4 μm in size was used as the shotcreting material, and the magnesia content was increased. This increase in magnesia content was also effective in securing the same expansion properties as those of the cast material. **Table 4** shows the properties of the ladle lining materials. Material with a moisture content of 7% was shotcreted onto ladles for minor repairs at amounts of 1.5 to 3 tons per ladle to a thickness of 30 to 40 mm. It exhibited good adhesion and low dust emission. With shotcreting of the new material, which is presently the normal practice, the lining life between two major repairs was extended from 180 to more than 200 heats.

2.5 Continuous Casting[16)]

In the continuous casting process, molten steel is poured from a ladle into a tundish and then through a tubular immersion nozzle into a casting mold to produce slabs, blooms or billets. Since tundish refractory is used as long as the immersion nozzle lasts, the life of a tundish/nozzle unit is determined by the wear of the nozzle at the flux powder line at the molten steel surface. A refractory material called ZG composed of zirconia, which is highly resistant to erosion by molten flux powder, with the addition of graphite is used for this nozzle portion.

The rate of erosion of ZG by the molten flux powder is generally considered to depend on the rate of the solution of zirconia particles in the liquid powder. The authors presumed that it depended on the rate of detachment of zirconia particles in the liquid from the outer surface of the nozzle, and using an equation of motion, estimated how far zirconia particles went from the outer surface that contacted the liquid of molten flux powder in oscillation. **Fig. 15** shows the distance of detachment of zirconia particles of different sizes from the nozzle outer wall with different viscosity of the liquid. As is clear from the graph, the lower the liquid viscosity and the larger the particle size, the quicker the particles detach from the wall surface, meaning that the quicker the material erodes.

Based on this result, the authors conceived an anti-erosion mechanism of immersion nozzles by forming a barrier of tightly packed zirconia particles at the outer surface contacting the molten powder, as schematically shown in **Fig. 16**.

In preparing test nozzles for trials on a commercial continuous caster, the mixing ratio of fine zirconia particles was increased as much as possible within the range to secure good resistance to thermal shock. When used for commercial casting operation, the developed nozzles withstood the thermal shock at the start of casting, and exhibited erosion indices about 30% lower than those of conventional ones. The outer surface of the developed nozzles after use was

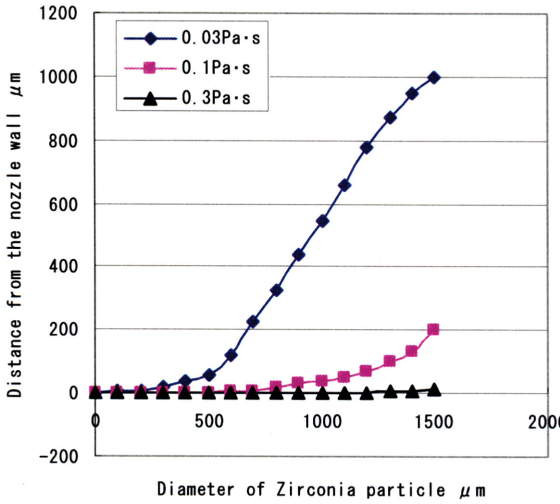

Fig. 15 Distance of zirconia particles from the nozzle wall as a function of diameter (300cpm)

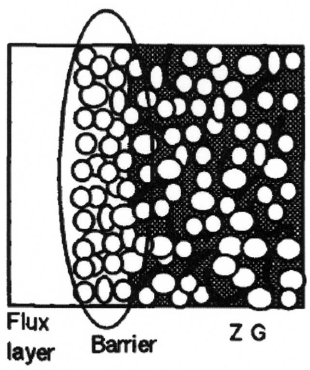

Fig. 16 Schematic illustration of barrier at nozzle outer surface

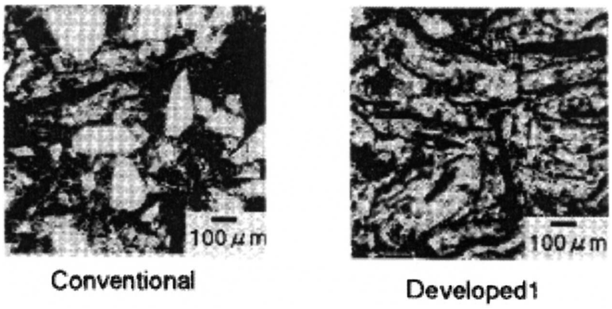

Fig. 17 SEM micrographs of polished surface of ZG refractories

smoother than that of conventional ones, evidencing less erosion. **Fig. 17** compares the structure of the developed nozzle after use with the same of a conventional one; the tightly packed barrier of fine zirconia particles of the developed nozzle is clearly seen here.

3. Closing

In response to the changes in steelmaking processes, refractory technology for steelmaking processes has developed dramatically over the last 25 years. This paper has presented some aspects of the development based on examples at Nippon Steel's Kimitsu and Muroran Works. Bearing in mind the need for high productivity, high product quality and low production costs required in steel production, the authors will continue to expend efforts on further technical improvements in refractory materials and work methods.

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