

SHINAGAWA TECHNICAL REPORT

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Technology

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品川技報

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要 旨

本報告は日本の一貫製鉄所における取鍋に適用される不定形耐火物の推移を取り纏め報告する。ジルコン質は流し込み材質として一定量の成果が得られた最初の材質であった。その後、取鍋で行われる2次精錬プロセスの過酷化に伴い、耐食性及び耐スラグ浸潤性を改善する為に、アルミナ・スピネル質、アルミナ・マグネシア質が開発された。現在、耐久性のある緻密質アルミナ・マグネシア質キャストブルが広く適用されており、良好な耐用性が得られている。

Abstract

This report summarizes the transition of monolithic refractory materials applied to steel ladles of Japanese integrated steel mills. Zircon castable was the first monolithic material that showed successful result. After that, in accordance with the intensification of secondary metallurgy carried out in steel ladle, dominant material has been changed to alumina-spinel followed by alumina-magnesia in order to improve resistance to corrosion as well as slag penetration. Currently, durable high density alumina-magnesia castable are widely applied and exhibits satisfying results.

1. はじめに

日本の多くの一貫製鉄所では、れんが工の深刻な人手不足が起こることを予見し、1970年代初頭から取鍋の内張りに不定形耐火物を採用している。以降、取鍋寿命の延長及び築炉工数、耐火物原単位、産廃処理量を削減するため、取鍋用キャストブルの技術革新が加速した。本報では、日本の一貫製鉄所の取鍋に使用された内張りキャスト

1. Introduction

Most of Japanese integrated steel mills have been adopting monolithic linings for steel ladles from the early 1970s according to the forecast of a serious shortage of skilled masons. Since then, technological innovations for steel ladle castables have been accelerated in order to reduce labor costs, refractory consumption,

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ブルの歴史を過去から現在の最新の技術に至るまでをレビューし紹介する。

2. 日本における取鍋不定形材質の変遷

2.1 黎明期

Table 1に施工方法の変遷をFig.1に流し込み材質の変遷を示す。

当初、取鍋は製鋼炉の溶鋼を造塊（铸造）作業場所へ運搬するための容器の一つであり、特に日本ではその内張材にろう石れんがやジルコンれんがが主に使用されていた。

1950年頃から進められた取鍋精錬（2次精錬）と、連続铸造法の普及拡大は溶鋼温度の上昇、滞留時間、精錬時間の増加、スラグ成分の高塩基度化等の変化をもたらした。これらは取鍋使用条件の過酷化に繋がり、内張り耐火物の高性能化が時代のニーズとなっていった¹⁻⁴⁾。

取鍋内張材の不定形化は施工の省力化を主目的に検討され、いくつかの製鉄所においてはスリッガー施工法が導入され、高珪酸材質及びジルコン質が適用されていたが設備面、環境面から汎用的な施工方法とは言えず普及には至らなかった⁵⁻⁷⁾。

1973年のオイルショックを契機に製造コスト低減が着目され、1979年から本格的に取鍋内張材の流し込み施工が開始された。概要をFig.2に示す。また1965年～1970年は全国各地に新鋭製鉄所が建設された時期でもあり、人手不足が社会問題と

and industrial waste. This report reviews the history of castables that have been applied to steel ladles of Japanese integrated steel mills and introduces state-of-the-art technology.

2. History of Ladle Castable Materials in Japan

2.1 Early dawn

Table 1 and Fig. 1 show the changes in the installation methods and ladle materials, respectively.

Originally, the ladle was one of the containers for transporting molten steel from the steelmaking furnace to the ingot casting facility. At that time, pyrophyllite brick and zircon brick were mainly used for the lining material in Japan. From around 1950, ladle refining (secondary refining) of molten steel and the continuous casting began to spread in order to produce high cleanliness steel with high efficiency. These steel making process innovations induced increases in molten steel temperature, residence time in steel ladle, refining time, and the basicity of slag, those are unfavorable status in terms of ladle refractory wear. Hence, development of durable ladle refractories have become a necessity of the times¹⁻⁴⁾.

Table 1 Changes in ladle materials and installation methods¹⁾

Period (year)	Refractory		Installation process	Remark
	Type	Materials		
- 1960	Brick	High Silicic (Pyrophyllite material) SiO ₂ : 65 - 75 %, Apparent porosity : 18 - 25 %	Brick	
1955 - 1965	Brick	High Silicic, Broaching properties SiO ₂ : 70 - 85 % Apparent porosity: 8 - 15 %	Brick	Other non-burned brick, SiC, High Alumina
1961 - 1975	Brick	Zircon, Semi zircon ZrO ₂ : 20 - 60 %	Brick	Dolomite brick
1971 - 1985	Monolithic	High Silicic, Zircon, Semi zircon, High Alumina	Slinger, Stamp vibration	
1979 -	Monolithic	Semi zircon, High Alumina, Spinel	Castable	

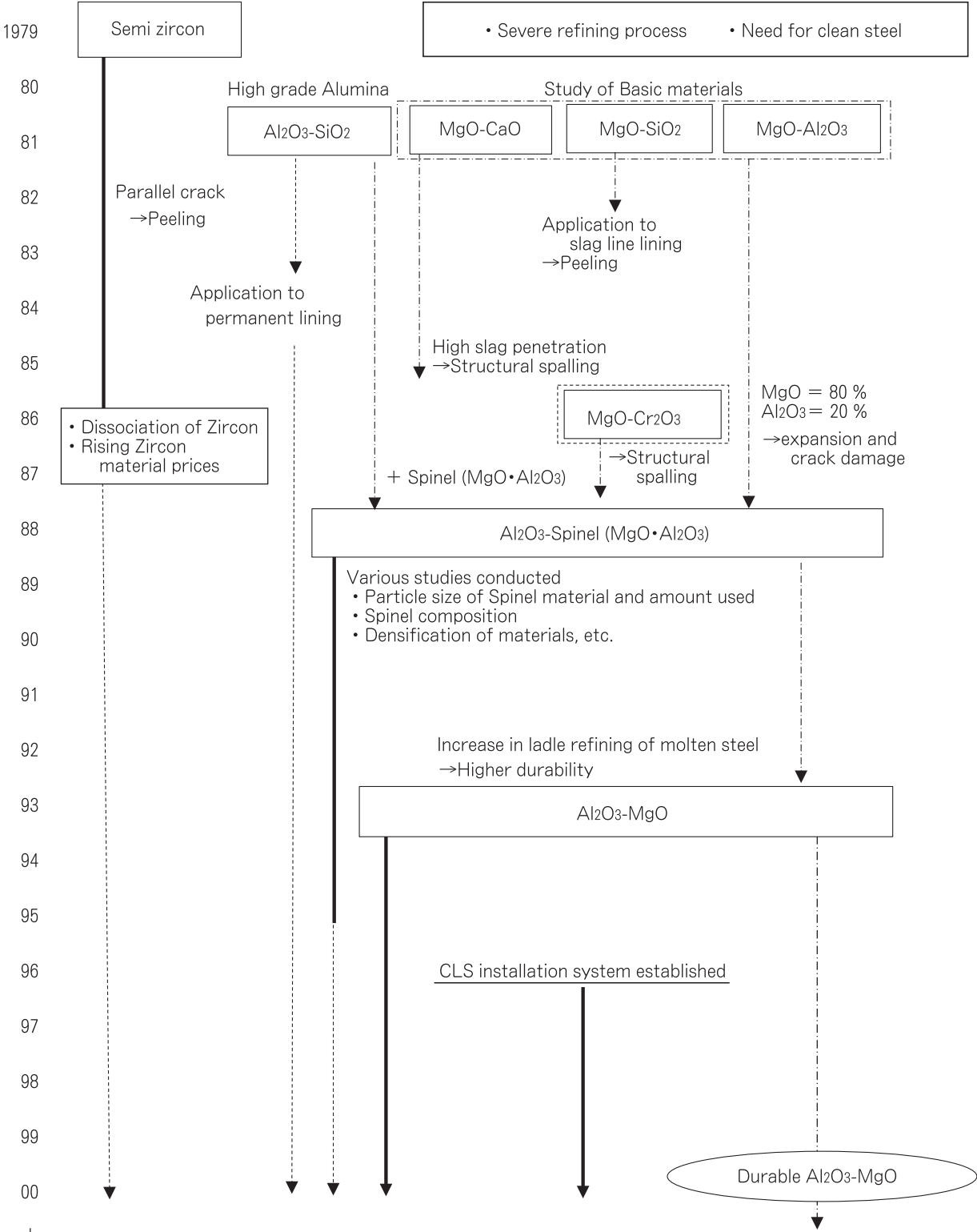


Fig. 1 Changes in ladle lining material (- 2000).

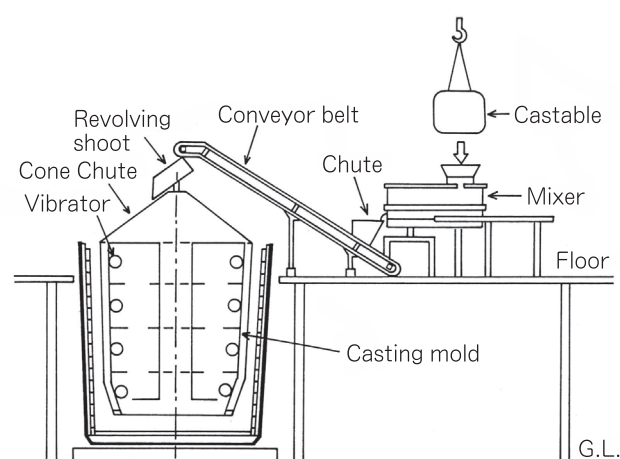


Fig. 2 Cast ladle lining installation system⁵⁾.

なった時代でもある。施工の省力化の観点から不定形耐火物が注目され各種検討が進んだ。

2. 2 ジルコン質キャストブル

流し込み材質はジルコン原料と珪石を配合したジルコン質から本格的に採用が進んだ。分散剤を活用する事により低水分で混練可能な低セメントキャストブル『CASTON : CST』が開発された。

また施工技術面ではバイブレーター等を用いた振動流し込み施工により緻密な施工体が安定して

On the other hand, monolithic ladle lining material was often examined mainly for reducing the labor required for installation. Temporarily, the slinger installation method was employed at some steelworks. For the method, high silicate material and zircon material were applied. While, it did not come into widespread use due to its specific installation method from the viewpoint of equipment and environment⁵⁻⁷⁾.

In 1973, the oil crisis took place. Since then, attention was paid to the reduction of manufacturing cost. Moreover, in the period between 1965 and 1970, several numbers of steel mills were built around Japan as shown in Fig. 2, which implied that the shortage of human resources became a social problem. From the viewpoint of installation labor saving, the monolithic refractory attracted attention. Therefore, monolithic ladle projects were started earnestly in 1979 followed by various examinations.

2. 2 Zircon material

The first material adapted for monolithic ladle was zircon castable. It is composed of zircon and quartzite, both of which are raw materials obtained as natural resources. Additionally, low-cement castable technology “CASTON : CST” was also applied. It is the technology utilizing a suitable deflocculant in order to reduce mixing water required for sufficient flowability of mixture so as to decrease the porosity of installed body. Furthermore, vibration casting technology developed at installation site allowed to cast the less water content-poor flowability mixture, resulting in further densification⁸⁾.

Adding to the densification, optimizations of material design also improves the corrosion resistance. For example, increasing zircon content is effective as shown in Fig. 3⁹⁾. While, if zircon fraction exceeds certain value, peeling wear tends to occur. This critical zircon fraction varies according to the operating condition,

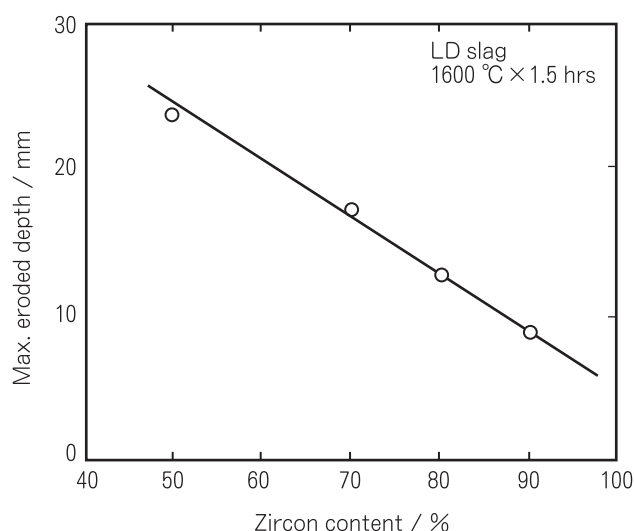


Fig. 3 Effect of zircon content on slag resistance⁹⁾.

得られるようになり多くの製鉄所で採用が進んだ⁸⁾。

ジルコン質流し込み材の耐食性はジルコン含有量の増加により向上する⁹⁾ (Fig.3)。そのため取鍋の作業条件や適用部位によりジルコンの含有量を選択する必要がある。溶損と剥離の関係を整理するとFig.4のような最小の損傷速度があると考えられる。この極小点は温度が高く、スラグの影響が大きいときジルコンリッチ側に移動する。ジルコン含有量の好適値はメタルライン部で70～75%，スラグラインで90～95%であると考えられ、適用部位に応じた調整が行われた。

同材質系には構造スポーリングによる剥離損傷の発生も見られていた。これらの原因を焼結層と施工体内部との間に生じる熱応力によるものと考え、背面温度域である1000℃加熱後の強度を向上させ稼働面付近の温度域である1500℃との強度ギャップを低減する検討が行われた。その取り組みの中でバインダーにコロイダルシリカを適用したケミカルバインダータイプ『CHEMICAST : CCT』が開発された。CCTは背面強度の向上と合わせてセメントレス化が得られ、セメント由来の

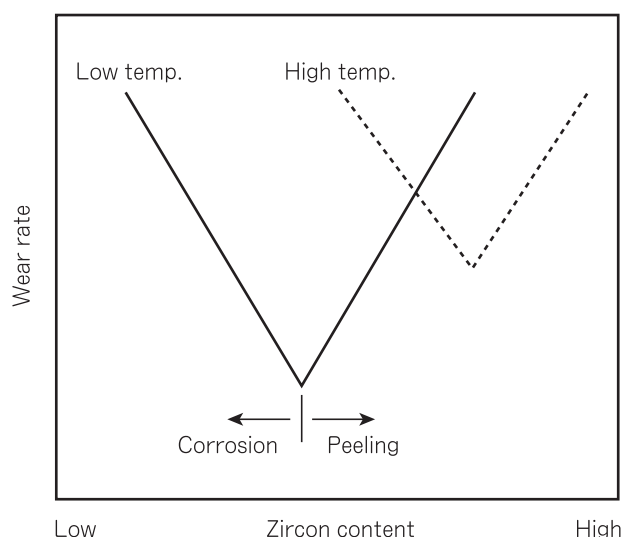


Fig. 4 Effect of zircon content on wear rate of zircon-silica castable : minimum value is determined from view point of corrosion and peeling⁹⁾.

i.e., it moves zircon rich side as temperature and/or slag corrosiveness increase (Fig. 4). Thus, optimum zircon fraction should be determined taking operating condition into account. Empirically, the preferable value of the zircon content was considered to be 70 to 75 % in the metal line portion and 90 to 95 % in the slag line

For the zircon material, peeling damage due to structural spalling was also observed. It is assumed to be induced by the thermal stress generated according to the difference in structural rigidity between high strength-surface sintered layer and low strength-inside layer, where the temperatures are estimated at 1500 °C and 1000 °C, respectively. Thus, researches were conducted to improve the strength after heating at 1000 °C.

Thanks to the various effort, chemical binder technology “CHEMICAST : CCT”, in which colloidal silica was applied as the binder, was invented. The CCT is the cement-less castable that exhibits high strength at relatively low temperature range and alumina cement-excluding composition suppresses the dissociation of zircon by cement-derived alumina. Our typical materials, which were developed based on these studies, are exemplified in Table 2.

In conjunction with the monolithic material technology improvement, many installation technologies were also developed. Among them, one of the characteristic method is endless installation by additional installation, which is the repetition of surface altered layer demolition and reinstallation¹¹⁾. As shown in Fig. 5, after the removal of the adhered slag, slag penetrated layer, and the sintered layer by a slag dresser, additional reinstallation is carried out. Ideally, the process can be repeated endlessly.

Figure 6 shows a comparison of ladle refractory cost in terms of installation methods, i.e.,

Table 2 Zircon materials

Material / Brand name		Zircon				
Item		CST-ZL-2	CST-Z71	CSZ17-BRX1B	CCT-Z63	CCT-Z52
Chemical composition / mass%	SiO ₂	37	40	52	37	47
	ZrO ₂	60	54	46	60	50
Liner change / %	After drying	-0.03	0.00	-0.03	0.0	0
	After heating 1000 °C - 3 h	0.20	0.00	0.49	0.19	0.66
	After heating 1500 °C - 3 h	0.50	0.00	2.74	1.22	1.09
Modulus of rupture / MPa	After drying	2.5	2.9	3.6	4.4	5.6
	After heating 1000 °C - 3 h	2.9	3.8	1.6	4.2	2.9
	After heating 1500 °C - 3 h	7.8	12.7	2.9	5.2	2.5
Cold crush strength / MPa	After drying	9.8	12.3	18.5	19.6	34.3
	After heating 1000 °C - 3 h	35.3	31.4	24.2	36.3	61.7
	After heating 1500 °C - 3 h	44.1	61.7	21.3	48.0	45.1
Apparent porosity / %	After drying	19.5	15.9	15.3	13.0	13.4
	After heating 1000 °C - 3 h	22.0	20.5	20.0	18.1	18.1
	After heating 1500 °C - 3 h	21.2	18.0	21.6	18.5	17.2
Bulk density	After drying	3.49	3.25	3.16	3.48	3.25
	After heating 1000 °C - 3 h	3.45	3.19	3.06	3.49	3.16
	After heating 1500 °C - 3 h	3.49	3.22	2.92	3.41	3.16
Water content / %		4.5	4.5	4.7 - 5.8※	2.0 + Binder : 3.5%	3.0 + Binder : 3.5%
Remark		ML	Bottom	ML Water : Binder = 5 : 1	SL Bottom	ML

アルミナによるジルコンの解離を抑制する働きもあった。

これら検討を基に開発された当社の代表的な材質をTable 2に示す。

材料の開発と合わせて使用方法でも耐火物のコスト削減の取り組みが実施された。中でも特徴的なのが継ぎ足し施工によるエンドレス施工である¹¹⁾。Fig.5に示すように修理落ちすると、スラグドレッサーで耐火物表面のスラグ及びスラグ浸潤層と焼結層を除去した後、継ぎ足し施工し作業を実施、同プロセスを繰り返す。

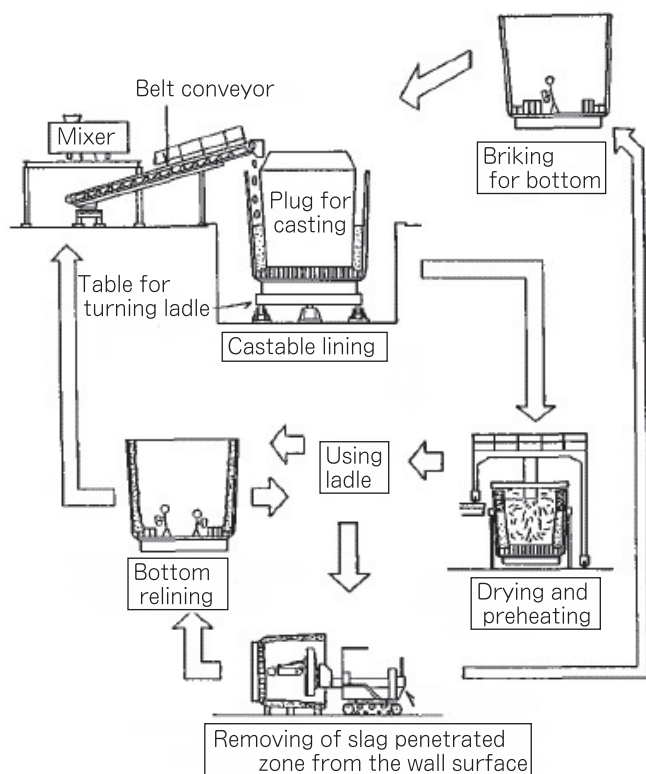
Fig.6にれんが施工鍋と流し込み施工鍋及び継ぎ足し施工を行った場合の耐火物コストを示す。継ぎ足し施工を行った場合れんが施工と比較して約18%コストを削減する事ができた¹¹⁾。

ジルコン質は比較的弾性率が低い材質であり、

brick lining, monolithic lining and monolithic relining with additional installation. It shows that additional installation achieves approximately 18 % cost reduction compared with brick construction¹¹⁾.

As generally agreed, zircon material has good heat spalling resistance due to a relatively low elastic modulus and high volume stability. In addition, the strength of the slag penetration layer and the sintered layer were low enough for easy dismantling, which is considered to be suitable for additional installation.

However, the situation has changed. The metallurgical treatment became more and more intensive, hence, further improvement was required for zircon castable. At that time,

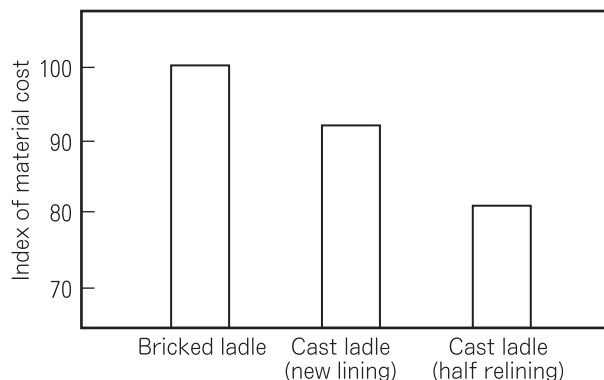
Fig. 5 Outline of castable lining method¹¹⁾.

また容積安定性が高いという特性から熱スポーリング性が良好な材質であると言える。またスラグ浸潤層、焼結層の強度も低く解体が容易であるため継ぎ足し施工に適していたと考えられる。

しかし取鍋精錬の過酷化による高耐用化の要望及び鋼品質の高級化指向、さらにはジルコン原料の高騰により、高アルミナ系にシフトしていく。近年でも特定の鋼種用にジルコン質が内張材に適用される場合もあるがその使用量は少なくなっている。

2. 3 アルミナ・スピネル質

1980年代後半になるとポストジルコンキャストブルの機運の高まりから、塩基性材質を中心に各種新規材質 (MgO-SiO_2 , $\text{MgO-Al}_2\text{O}_3$, MgO-CaO , $\text{MgO-Cr}_2\text{O}_3$, $\text{Al}_2\text{O}_3\text{-SiO}_2$) の検討が相次いだ¹²⁻¹⁷⁾。しかし、いずれの材質も抜本的な対策にならず、取鍋内張材として定着には至らなかった。その後同時期に検討されていた材質の中からアルミナ・スピネル質の優位性が見いだされ、同材質系の研究開発が進んだ¹⁸⁻²³⁾。

Fig. 6 Comparison of consumption¹¹⁾.

market price of zircon increased tremendously. According to these factors, a shift to a high alumina material became a major trend. In recent years, the application of zircon material has been decreasing. It is used to the ladle for specific steel production.

2. 3 Alumina-spinel material

In the late 1980s, due to the increasing demands for post-zircon castable, various new materials (MgO-SiO_2 , $\text{MgO-Al}_2\text{O}_3$, MgO-CaO , $\text{MgO-Cr}_2\text{O}_3$, $\text{Al}_2\text{O}_3\text{-SiO}_2$) were investigated¹²⁻¹⁷⁾. All of them but $\text{Al}_2\text{O}_3\text{-SiO}_2$ material were the materials containing basic compounds. However, none of these materials became popular according to their insufficient performance. Subsequent to the period, the superiority of alumina-spinel material, which had once been examined, was reconfirmed. Thus, research and development of the alumina-spinel system have been progressed¹⁸⁻²³⁾. At that time, studies were conducted using stoichiometric spinel that composed of $\text{Al}_2\text{O}_3 : \text{MgO} = 70.2 : 28.6$ as raw material²⁴⁾.

Figure 7 shows the variation in the depth of corrosion and slag penetration as a function of spinel amount included in castable evaluated for the specimens after the slag corrosion test. The depth of corrosion is expressed as an index of

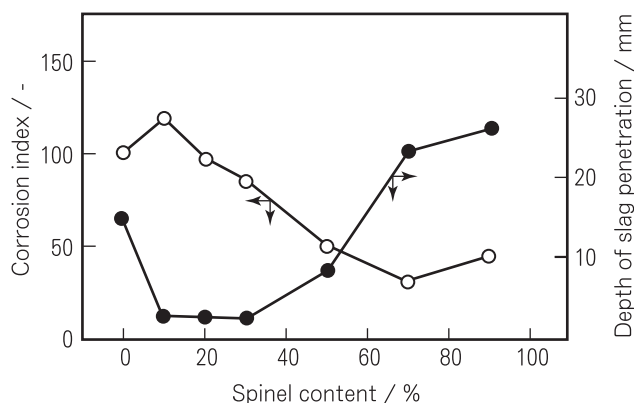


Fig. 7 Relation between spinel content and corrosion resistance²⁴⁾.

$\text{Al}_2\text{O}_3 : \text{MgO} = 70.2 : 28.6$ のスピネル原料を用いた検討が行われた²⁴⁾。

Fig.7にスピネル添加量と溶損深さ及びスラグ浸潤深さの関係を示す。溶損深さはスピネル無添加の試料を100として指数表示した。溶損深さはスピネル添加量が増加すると小さくなる傾向を示す。一方、スラグ浸潤深さは添加量が10%-30%の範囲までは小さくなる。しかし添加量が50%以上では逆に大きくなり構造スポーリングが起きると考えられた。

森ら²⁵⁾はマトリックスと浸潤スラグ成分の反応による粘性の変化によるスラグ浸潤抑制のメカニズムを報告している。Fig.8に概念図を示す。 CaO-FeO-SiO_2 系のスラグは、マトリックス中へ浸透していく。浸透成分中のCaOは、主に Al_2O_3 と反応して、 CA_6 などのCaO- Al_2O_3 系鉱物を生成する。またFeOは主にスピネル中に固溶していく。スラグ成分は浸透が進むに従って、 SiO_2 リッチな組成に変化していく。この SiO_2 に富む液相は、粘稠な組織になり、スラグ浸透が抑制される。

更に浅野ら²⁵⁾の検討によると、スピネルは Al_2O_3 を固溶し、 Al_2O_3 リッチな陽イオン欠陥を伴った格子欠陥型スピネル ($\text{MgO} \cdot n\text{Al}_2\text{O}_3$) を生成する。スラグ中のFeOは、格子欠陥型スピネル固溶体の空孔となっている陽イオン位置に侵入する。

これら材料内部における反応の相乗効果により、アルミナ・スピネル質流し込み材のスラグ浸潤は抑制されると考えられた。

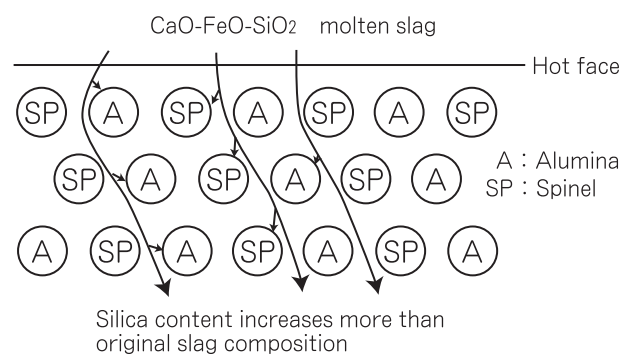


Fig. 8 Schematic expression of the slag penetration into the spinel added alumina castable²⁵⁾.

100 for the sample to which no spinel is added. The depth of corrosion tends to decrease as the amount of spinel increases. On the other hand, the slag penetration depth showed minimum value for the range of 10 % to 30 % of the spinel amount. Hence, structural spalling is concerned if it includes more than 50 % of spinel because of significant increase in slag penetration depth.

Mori et al.²⁵⁾ explained the mechanism of slag penetration inhibition effect of spinel addition by viscosity changes due to simultaneous reactions among Al_2O_3 matrices, spinel particles and penetrated slag components. Figure 8 shows a conceptual diagram of which the slag of the CaO-FeO-SiO_2 system penetrate into the matrices. In this system, CaO in the penetration components reacts primarily with Al_2O_3 to form $\text{CaO-Al}_2\text{O}_3$ minerals such as CA_6 and fixed. Meanwhile, FeO fixed in spinel to form solid solution. As a result, the composition of the slag changes to SiO_2 rich. The SiO_2 rich liquid phase exhibits high viscosity so that further slag penetration is suppressed.

Asano et al.²⁵⁾ pointed out that stoichiometric spinel turns to a spinel solid solution with cation defect ($\text{MgO} \cdot n\text{Al}_2\text{O}_3$) as a result of the reaction with Al_2O_3 prior to the slag penetration. The FeO in the penetrated slag occupies the cationic

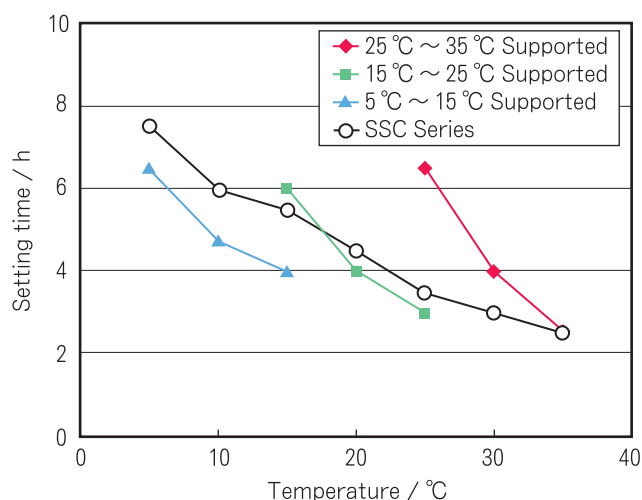


Fig. 9 Relationship between temperature and setting time.

その後上記知見を基に Al_2O_3 リッチ組成スピネル原料を用いた検討が進められた。更にセメントとの反応によりスラグの浸潤抑制に必要なアルミナ微粉が相当量消費されていることから、微粉部をアルミナリッチな組成に維持することがスラグ浸潤抑制に対して重要であると報告されている²⁷⁾。

一方、不定形の普及に従い施工の安定性にも強い関心が寄せられるようになった。特に可使時間及び硬化時間の制御、耐爆裂性の担保は重要な点である。

これら市場のニーズを受けて、『Super-Shiro-Cast : SSC』が開発された。SSCは硬化の温度依存性が非常に小さい特徴があり、硬化調整が不要で5℃から35℃の幅広い温度域に施工対応が可能なバインダーシステムである。温度と硬化時間の関係をFig.9に示す。

SSCシリーズは施工トラブルのリスクが少なく作業者の作業負荷軽減及び施工の安定性向上に大きく寄与した。代表的なアルミナ・スピネル材質をTable 3に示す。

また取鍋の寿命向上に向けた操業側の改善も行われており、特に蓋掛け率の向上は取鍋寿命延長に寄与した。蓋掛け率と取鍋寿命の関係をFig.10に示す²⁸⁾。メーカーとユーザーの相互的な取り組

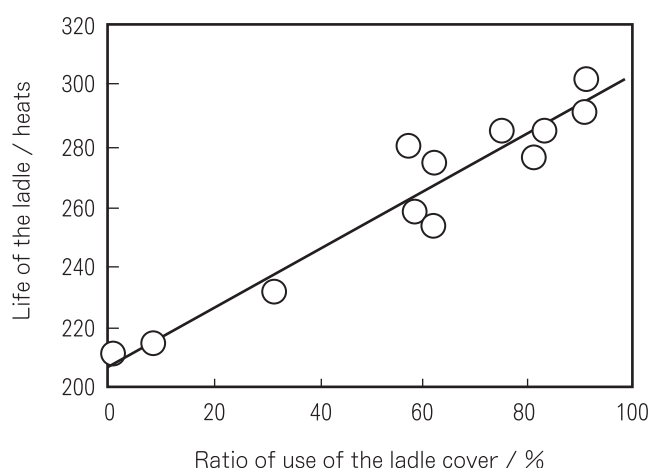
position, which is the vacancy of the lattice defect type spinel solid solution. Thus, the slag penetration of the alumina-spinel system was considered to be suppressed by the synergistic effect of the reaction occurring inside of these materials. Based on the above hypothesis, studies using Al_2O_3 -rich spinel as raw materials were carried out. Furthermore, since a considerable amount of alumina fines, which are required to suppress the slag penetration, tends to be consumed by reacting with alumina cement, maintaining the sufficient amount of alumina fines is crucial.

In accordance with the generalization of monolithic applications, stability of installation became the one of the main topic. In particular, controlling the working time and setting time, and ensuring explosive spalling resistance are essential. In response to the needs, “Super-Shiro-Cast: SSC” were developed. SSC is characterized by small susceptibility of setting time to temperature, which is attributed to a unique binder system. Therefore, it is applicable to the installation at a wide temperature range of 5℃ to 35℃ without on-site setting time adjustments. The relationship between temperature and setting time is shown in Fig.9. The SSC series reduced the risk of installation trouble and greatly contributed to the reduction of the workload of the operator, resulting in the improvement of installation efficiency. Typical alumina-spinel materials are shown in Table 3.

In addition, improvement in operational measures to lengthen the service life of the ladle was also carried out. In particular, the improvement of the lid covering rate contributed to the extension of ladle life significantly. Figure 10 shows the relation between the covering rate and ladle life²⁸⁾. It should be noted that successful application of alumina-spinel material was attributable to mutual efforts of manufacturers

Table 3 Alumina spinel materials

Material / Brand name		Alumina - spinel				
Item		SSC-A9011	SSC-AS101	SSC-AS115	SSC-AS107	CH18-MS65-A-R
Chemical composition / mass%	Al ₂ O ₃	90	94	94	88	91
	MgO	7	3	4	10	5
Liner change / %	After drying	-0.06	-0.03	-0.03	-0.03	-0.06
	After heating 1000 °C - 3 h	-0.09	-0.03	-0.03	-0.03	0.00
	After heating 1500 °C - 3 h	0.31	0.12	0.12	0.12	0.96
Modulus of rupture / MPa	After drying	7.4	3.8	4.2	6.2	5.8
	After heating 1000 °C - 3 h	8.3	5.5	5.5	3.7	3.4
	After heating 1500 °C - 3 h	21.1	18.1	17.9	13.5	15.1
Cold crush strength / MPa	After drying	27.5	28.2	28.3	35.8	39.4
	After heating 1000 °C - 3 h	35.3	53.1	47.2	48.9	29.6
	After heating 1500 °C - 3 h	62.8	91.0	85.3	70.7	59.0
Apparent porosity / %	After drying	14.7	15.2	15.2	15.7	16.1
	After heating 1000 °C - 3 h	19.2	17.8	17.5	18.6	20.50
	After heating 1500 °C - 3 h	20.5	19.9	19.8	21.1	23.2
Bulk density	After drying	3.02	3.10	3.08	2.97	2.95
	After heating 1000 °C - 3 h	2.95	3.08	3.04	2.99	2.90
	After heating 1500 °C - 3 h	2.90	3.03	3.03	2.95	2.84
Water content / %		6.0 - 6.5	5.5 - 6.5	5.5 - 6.5	5.5 - 6.5	7.0
Remark		ML	ML	ML	Bottom	ML

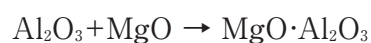
Fig. 10 Relation ship between ladle life and ladle cover use ratio²⁸⁾.

and users and it considerably contributed to the reduction of ladle cost.

2. 4 Alumina-magnesia material

2. 4. 1 Development of alumina-magnesia material

In the late 1990s, investigations of alumina-magnesia materials were advanced²⁹⁻³³⁾. The alumina-magnesia castable is a material consists of alumina raw material and magnesia fine powder. Both compounds react with each other during heating to generate secondary spinel according to the following equation.



Same as alumina-spinel material, this material system has also been tried during the period when alternative of zircon castable was

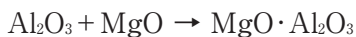
みによりアルミナ・スピネル質は幅広く適用され取鍋原単価の低減に大きく貢献した。

2. 4 アルミナ・マグネシア質

2. 4. 1 アルミナ・マグネシア質の開発

1990年代の後半になるとアルミナ・マグネシア質の検討が進んだ²⁹⁻³³⁾。

アルミナ・マグネシア質キャストブルはアルミナ原料とマグネシア微粉を組み合わせた材質であり、加熱時にこの両者が反応して、以下の式に従い2次スピネルを生成する。



取鍋の内張材としてジルコン質の代替材質としても適用が試みられてきた材質の一つであるが反応により生成するスピネルの異常膨張や組織脆化により、熱的スポーリングが発生しやすい傾向があり定着しなかった。

マグネシア微粉の適正な添加量とシリカ系超微粉の少量添加により熱膨張挙動を制御できると同時に応力緩和能力に優れた材質設計を可能とした。

Fig.11に荷重下における熱間膨張曲線を示す。アルミナ・マグネシア質キャストブルはアルミナ・スピネル質キャストブルと比較して荷重下での変形能力を有している。

Fig.12にアルミナ・マグネシア質キャストブル

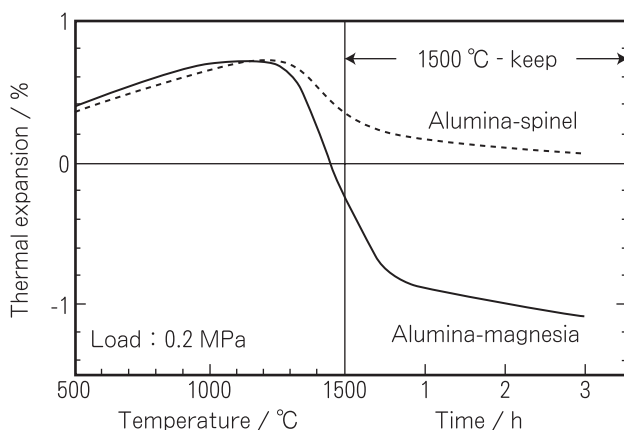


Fig. 11 Thermal expansion curve under load⁵⁾.

explored. However, the result was insufficient according to the thermal spalling caused by rapid expansion and structure deterioration, both of which were resulted from the in-situ spinel formation reaction.

Several years later, thermal expansion-controlling technology for alumina-magnesia castable was invented. It is achieved by adjustment of amount of magnesia powder and silica fine powder. In addition, according to this technology, the suitable stress relaxation ability at high temperature can be obtained. Figure 11 shows the comparison of thermal expansion curve under load between alumina-magnesia material and alumina-spinel material. Alumina-magnesia material shows the larger ability to deform under load compared to alumina-spinel material.

Figure 12 shows the relationship between the magnesia content and corrosion resistance of alumina-magnesia material. The corrosion resistance becomes better as the content of magnesia increases. On the other hand, slag penetration is minimized with a magnesia content range of between 5 to 10 %. In general, alumina-magnesia material has better slag

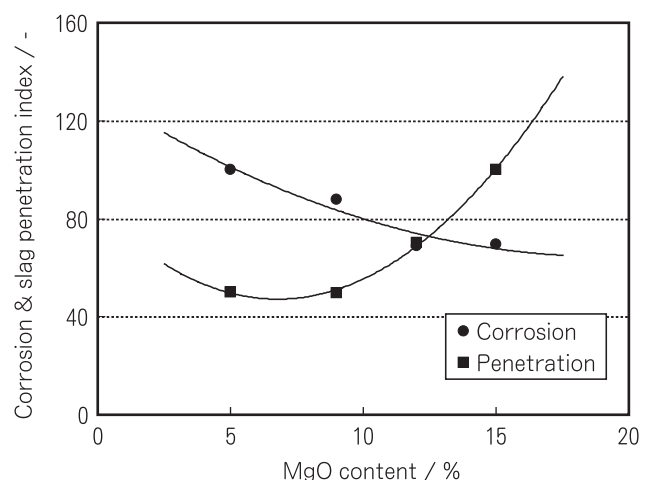


Fig. 12 Relation between MgO content and corrosion and penetration³⁵⁾.

のマグネシア含有量と耐食性の関係を示す。耐食性はマグネシアの含有量の増加に伴い良好になる。一方スラグの浸潤量はマグネシアの含有量が5～10%の範囲が最も少なくなる。

一般的にアルミナ・マグネシア質キャストブルは合成されたスピネルを添加するアルミナ・スピネル質キャストブルよりも非常に細かいスピネルが均一にマトリックスへ分散しているため耐食性・耐浸潤性が向上すると考えられている。またスピネル生成時に膨張を伴うため、拘束下では材料の緻密化が起こることも影響している。

これら良好な特性から実機への適用が進み、取鍋寿命が向上した。

また側壁部においては炉代間寿命延長による原単価低減を目的に吹付補修材の検討も行われている。流し込み施工と同等の緻密な組織が得られるショットクリート工法『Clean-shot : CLS』が主に適用されている。装置の概要をFig.13に示す。一時期は、自動施工システムの開発を行い、取鍋内張りを自動で施工するロボッティング技術も確立された (Fig.14)。現在では各所で採用が進み、取鍋補修方法の一つとして確立された技術となっ

corrosion and penetration resistance than alumina-spinel material. This is attributable to the difference in spinel distribution status, i.e., alumina-magnesia castable includes evenly-dispersed very fine secondarily spinel formed by in-situ reaction in the matrix, while alumina-spinel material contains courser spinel grains that had been previously synthesized as refractory raw materials. Furthermore, superior corrosion resistance of alumina-magnesia material is resulted from densification according to the restraint of large expansion caused by in-situ spinel formation reaction.

Thanks to the excellent properties, ladle life was improved considerably. In addition, the shot repairing material has also been examined for side wall repair in order to reduce cost by extension of service life between major repairs. The shotcrete method “Clean-Shot : CLS”, which is the gunning repair being able to obtain almost equivalent dense structure as the casting method, is mainly applied. An outline of

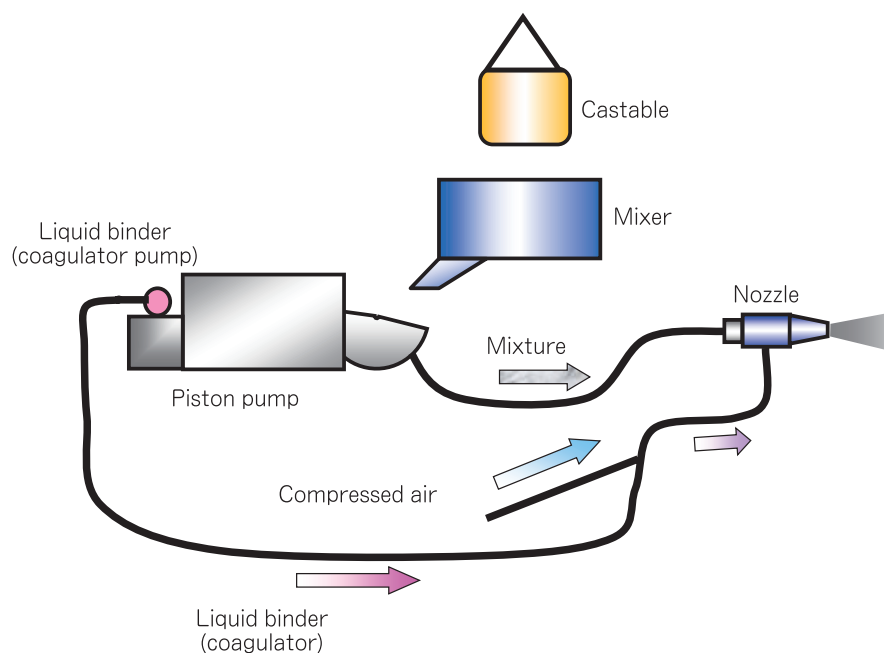
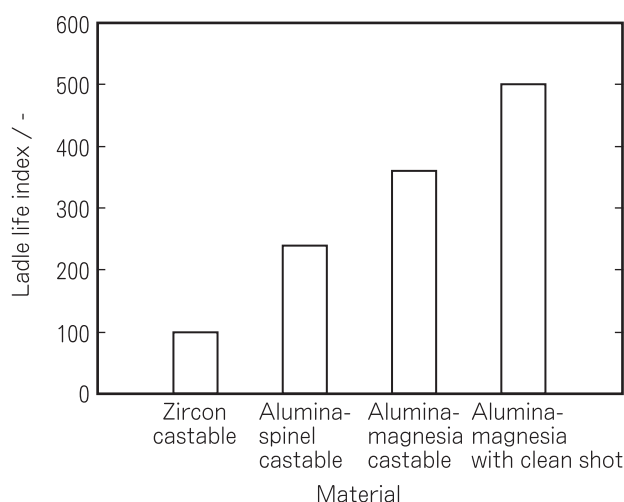


Fig. 13 Typical clean shot system.



Fig. 14 Automatic installation equipment.

Fig. 15 Change in monolithic ladle lining life at typical integrated steel mills in Japan⁵⁾.

ている。

Fig.15に取鍋ライニングと鍋寿命の推移を示す。CLS工法と組み合わせる事により、取鍋原単価の大幅な低減効果を得ることが出来た⁵⁾。

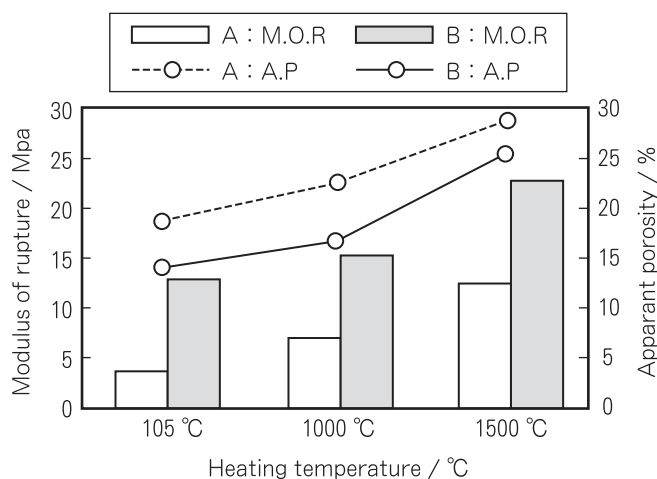
2. 4. 2 アルミナ・マグネシア質の最新技術

アルミナ・マグネシア質の基本的な配合設計は90年代後半には略完成しており、取鍋以外にもRH浸漬管の外周キャスタブル等への展開も図られた。また骨材にスピネル原料を適用したスピネル・マグネシア質も開発された³⁴⁻³⁵⁾。

取鍋内張材の更なる材質改善の方向性として緻密化の検討が進められた。佐々木ら³⁶⁻³⁷⁾は粒度構成を粗粒化し、低水分化する手法を報告している。

Fig.16に各焼成温度の曲げ強さと見掛け気孔率

Material・Name Item		Alumina-Magnesia	
		Sample A	Sample B
Chemical composition / mass%	Al ₂ O ₃	92	92
	SiO ₂	1	1
	MgO	5	5
Water content / %		5.5	4.2
Vibration flow values / (mm/5s)		195	190

Fig. 16 Change in monolithic ladle lining life at typical integrated steel mills in Japan³⁷⁾.

the equipment is shown in Fig. 13. A robotizing system for automatic installation of the ladle lining has also been established (Fig. 14). At present, it has been adopted at various places become an established technology as one of the ladle repair methods.

Figure 15 shows the changes in ladle lining and ladle life. The cost of ladles was significantly reduced by combining the CLS method⁵⁾.

2. 4. 2 The latest technologies for alumina-magnesia material

The basic formulation design of alumina-magnesia material was almost completed in the late 90s. Adding to steel ladle, the deployment of the materials to RH snorkel outer peripheral castable, etc. was also in progress. For the sake of further improvement, spinel-magnesia material in which spinel raw material is applied as an aggregate instead of alumina has also been developed³⁴⁻³⁵⁾.

の比較を示す。低水分材質は各温度とも曲げ強さが増加している。またこの材質をプレキャスト施工することにより更なる緻密化を図った。従来の施工水分が5.5%であるのに対して、緻密材質は4.2%、プレキャストブロック化により3.8%の水分量で施工を行った。

Fig.17にこれら材質の侵食試験結果を示す。低水分化に伴う緻密化により耐食性と耐浸潤性の改善効果が認められた。Fig.18はこれら材質を実機におけるネック部位の一つである取鍋湯当たり部へ適用した結果を示している。緻密化するに従い実機の損傷速度は低減傾向を示した。

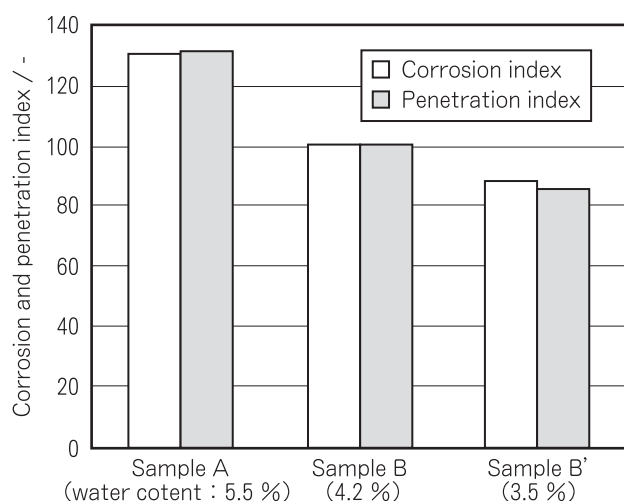


Fig. 17 Improvement in corrosion for higher density material³⁷⁾.

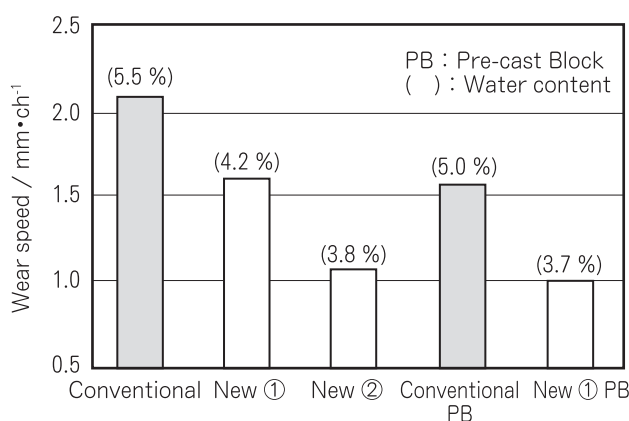


Fig. 18 Wear speed of LF ladle bottom impact area³⁷⁾.

Meanwhile, densification was investigated as a direction of further improvement of the ladle lining material. Sasaki et al.³⁶⁻³⁷⁾ reported that coarsening the particle size distribution is effective for reducing water content. Figure 16 shows the modulus of rupture and apparent porosity after firing at each temperature. The modulus of rupture of the low water material is larger at each temperature. Further densification was achieved by precasting this material. While the conventional water content was 5.5 %, that of the dense material was 4.2 %, and reduced further to 3.8 % when it is applied to manufacture the precast block products.

Figure 17 shows the results of the corrosion test of these materials. The improvements of the corrosion resistance as well as slag penetration resistance were achieved by the densification accompanying mixing water reduction. Figure 18 shows the results of applying these materials to the impact area of ladle, which is one of the neck portions in the actual ladle. The damage rate of the actual ladle tended to decrease as it became denser.

However, these techniques for reducing water content were limited to bottom of ladle or precasting because of their poor flowability, thus, it was difficult to generalize. Nishida et al.³⁸⁾ developed the low mixing water-dense materials with good flowability by optimizing the application of a high-performance defloculant. It enabled more generalized application of the dense alumina-magnesia castables.

Figure 19 shows the amount of water required for the mixture to show equivalent flowability, which is vibration flow value of 200 mm. The water addition of the developed material was decreased by more than 1.0 % compared with conventional material. Hence, it became possible to cast below 4.0 % water addition at the actual ladle. The properties of the dense castables

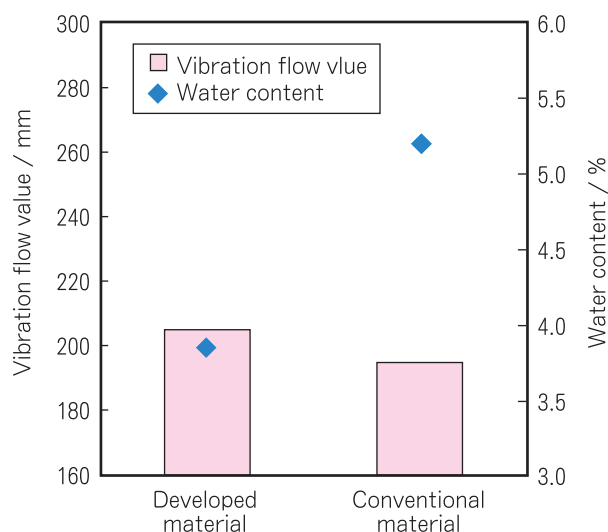


Fig. 19 Flow characteristics of material (vibration flow value)³⁸⁾.

しかしこれら低水分化の技術は流動性が低い事から取鍋の敷部もしくはプレキャストに限定されており，汎用的に適用可能な技術とは言い難い。そこで西田³⁸⁾らは高性能分散剤を適用し，汎用的に施工可能な緻密材質を検討した。

Fig.19に振動フロー200mmを目安に混練した際の添加水量を示す。従来材と比較して，1.0%以上の減水効果が認められ，添加水量4.0%以下の低水

are shown in Table 4. By decreasing the water addition, the modulus of rupture after heating below 1000 °C was increased. Consequently, the ratio of strength between samples heated at 1500 °C and samples heated at 1000 °C decreased by approximately 40 %. The corrosion and slag penetration resistance of the developed material was improved by 20 %. This was accomplished through densification (Fig. 20).

Figure 21 shows the damage rate of ML of in the actual ladle. As shown in Fig. 21, a service life improvement effect of approximately 30 % was obtained.

These dense alumina-magnesia material, which are called “High-Density-Castable : HiDeC” are currently being used in steel mills. Our main alumina-magnesia materials are shown in Table 5.

3. Summary

Technological innovation of monolithic materials for steel ladle has been promoted at integrated steel mills in Japan for the purpose of labor reduction and improvement of durability.

Table 4 Properties of materials³⁸⁾

Material		Developed material	Conventional material
Item			
Chemical composition / mass%	Al ₂ O ₃	92	92
	MgO	5	5
Permanent liner change / %	110 °C × 24 h	0.00	-0.03
	1000 °C × 3 h	0.05	-0.03
	1500 °C × 3 h	+1.94	+1.21
Modulus of rupture (Crush strength) / MPa	110 °C × 24 h	12.2 (49.7)	5.9 (30.8)
	1000 °C × 3 h	12.6 (64.4)	6.2 (52.4)
	1500 °C × 3 h	27.3 (72.2)	24.0 (65.1)
Apparent porosity / % (Bulk density)	110 °C × 24 h	10.9 (3.27)	14.3 (3.21)
	1000 °C × 3 h	14.1 (3.25)	16.4 (3.19)
	1500 °C × 3 h	17.9 (3.10)	19.8 (3.00)
Water content / %		3.5 - 4.5	5.0 - 6.0

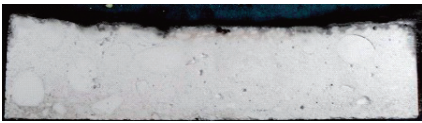
	Cross section	Corrosion depth (Penetration depth)
Developed material		10.1 mm (5.3 mm)
Conventional material		12.4 mm (6.7 mm)

Fig. 20 Result of slag test (1650 °C - 4 h, C/S=3.3)³⁸⁾.

分施工が可能な流動性を実現した。品質特性を Table 4に示す。低水分化することにより1000℃での強度向上が認められ、1000℃と1500℃の強度ギャップについても約40%低減したことから、実機での剥離抑制効果が期待される。またFig.20に示す侵食試験結果では緻密化の効果により耐食性、耐浸潤性で約20%の改善効果が得られた。

Fig.21に実機取鍋MLにおける損傷速度を示す。損傷速度では約30%の耐用性向上効果が得られた。

これら緻密質アルミナ・マグネシア質キャストブルは『High-Density-Castable: HiDeC』と呼称し、現在各所製鉄所で適用され使用されている。当社の主なアルミナ・マグネシア材質をTable 5に示す。

3. まとめ

日本国内の一貫製鉄所において、省力化、耐用性向上を目的に取鍋用流し込み材の技術革新が進んだ。れんが→ジルコン質→アルミナ・スピネル質→アルミナ・マグネシア質という材質の変遷を経て高性能アルミナ・マグネシア質（低水分化）に至っている。

温度依存性が少ないバインダーシステム及び緻密質材質は当社固有の技術であり、国内で広く使用されている。

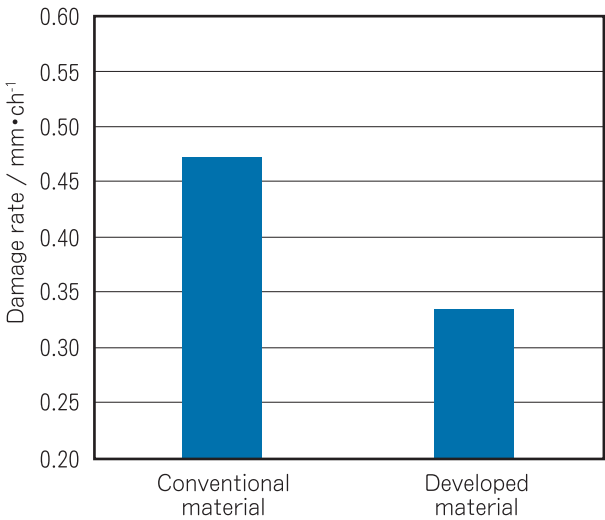


Fig. 21 Damage rate³⁸⁾.

The transition of brick → zircon material → alumina-spinel material → alumina-magnesia material has led to low mixing water-high performance alumina-magnesia material. In specific, less temperature dependent binder systems and dense materials are our unique technology and are widely used in Japan.

4. Closing

The damage mechanism of the ladle lining material is shown in Fig. 22. The main damage factors are peeling by cracking and wearing. Wearing includes chemical wear damage and physical wear damage. Theoretically, it may

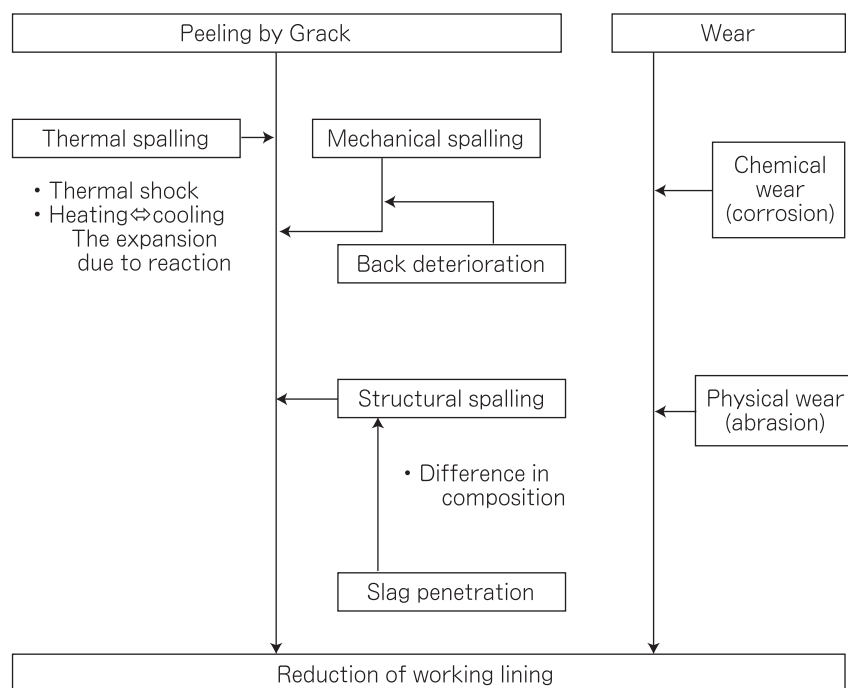


Fig. 22 Steel ladle lining damage factors.

Table 5 Alumina Magnesia materials

Material / Brand name Item		Alumina-Magnesia				Spinel-Magnesia
		SSC-AM260	SSC-AM625	CH18-M2S-BR-SR-121	SSC-AM426	SSC-SM185
Chemical composition / mass%	Al ₂ O ₃	92	93	90	92	90
	SiO ₂	1	1	1	1	1
	MgO	6	5	7	6	7
Liner change / %	After drying	-0.03	-0.02	0.00	-0.04	-0.02
	After heating 1000 °C - 3 h	-0.03	-0.09	0.00	-0.09	-0.04
	After heating 1500 °C - 3 h	1.21	1.79	2.20	1.20	1.27
Modulus of rupture / MPa	After drying	5.9	5.5	7.4	8.3	6.7
	After heating 1000 °C - 3 h	6.0	6.7	6.6	16.0	8.4
	After heating 1500 °C - 3 h	13.2	22.8	21.1	33.1	15.4
Cold crush strength / MPa	After drying	20.5	26.8	32.5	43.3	37.0
	After heating 1000 °C - 3 h	32.4	45.3	22.1	80.6	53.0
	After heating 1500 °C - 3 h	55.1	97.9	74.2	89.3	84.8
Apparent porosity / %	After drying	14.7	15.7	16.6	12.7	13.5
	After heating 1000 °C - 3 h	16.8	18.3	19.4	15.9	16.2
	After heating 1500 °C - 3 h	20.5	19.9	23.5	18.8	18.8
Bulk density	After drying	3.18	3.11	3.08	3.22	3.12
	After heating 1000 °C - 3 h	3.15	3.06	3.06	3.21	3.08
	After heating 1500 °C - 3 h	3.00	2.88	2.87	3.08	3.00
Water content / %		5.0 - 6.0	3.8 - 4.8	5.0±0.5	3.8 - 4.8	4.5 - 5.0
Remark		ML	Bottom	ML	ML HiDeC	ML

4. おわりに

取鍋内張材質の損傷機構をFig.22に示す。

取鍋の部位や操業条件により支配的要因は異なると考えるが、主な損傷要因としては亀裂による剥離と溶損がある。溶損には化学的な損傷と物理的な摩耗がある。近年実機における損傷は剥離が主体であると考え。主な剥離の種類として、熱スポーリングと構造スポーリング、機械的スポーリングがあり、実機においてはそれぞれの要因が相互的に作用し損傷に繋がると考える。

昨今の取鍋内張材の配合技術としては、実機条件への調整の精度が取鍋安定操業に向けた重要な課題であると考え。合わせて新材質また、高付加価値を有する材質の登場が業界でも望まれている。

differ depending on the part of the ladle and the operating conditions. In recent years, however, it is widely agreed that the dominant damage factor of the actual ladle is peeling resulted from cracking. Generally, the cause of cracking is classified into thermal spalling, structural spalling, and mechanical spalling. In the case of steel ladle refractories, the interaction among the factors is assumable.

In recent years, the accuracy of adjustment of lining materials to fluctuations in actual ladle conditions is considered to be an important issue for stable operation of the ladle. In addition, the development of new materials and high value-added materials are also desired in the industry.

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