

SHINAGAWA TECHNICAL REPORT

各用途に適合した取鍋用煉瓦

Ladle Brick Lineup Suitable for Several
Applications

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品川技報

報文 REPORT

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要 旨

搬送容器および精錬時の溶鋼保持容器として使用される取鍋の内張り煉瓦はその取鍋の用途や製造する鋼の品質などにより様々な特性が要求される。当社の特徴ある取鍋煉瓦を取鍋の用途に合わせて紹介する。

Abstract

Steel ladles are the vessels that retain a molten steel temporarily to transfer it to steel casting facilities. Ladle bricks, which are installed inside the steel ladles, are required to have various characteristics depending on the application of the ladle and the quality of the steel to be produced. In this article, our distinctive ladle bricks for ladle applications are introduced.

1. はじめに

本邦の高炉メーカーでは1970年代に取鍋用耐火物の施工省力化を目的として敷やメタルライン用耐火物の不定形化が進んだ。一方、国内電気炉メーカーや海外の製鉄所ではワーク耐火物に各種の定形煉瓦を使用している場合が多い。

一般に製鋼過程において取鍋は転炉や電気炉で精錬された溶鋼を搬送するだけでなく、温度補償や成分調整を目的に行う二次精錬の反応容器として使用されるが、使用する設備や溶製する鋼種、操業の要求はそれぞれ異なっており、そのニーズは多岐にわたる。

本報では代表的な例としてカーボンピックアップ

1. Introduction

In the 1970s, integrated steel mills in Japan made progress in changing steel ladle refractories from shaped bricks to monolithic refractories for the purpose of reducing refractory-installation labor. On the other hand, domestic electric arc furnace-based mini mills and overseas steel mills often use various kinds of bricks for the wear lining of the ladle. In the steel making process, ladles are generally used not only to transfer molten steel refined in converters or electric arc furnaces, but also as reaction vessels for secondary refining for

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プを極度に嫌う極低炭素鋼溶製用の取鍋, LFやRHなどの一般的な二次精錬を行う取鍋, 熱ロスや臭気に対して配慮が必要な取鍋を取り上げ, それぞれについて適用が推奨される煉瓦のラインナップを紹介する。

2. 精錬取鍋用煉瓦のラインナップ

2. 1 極低炭素鋼を溶製する取鍋

極低炭素鋼を製造する取鍋では高温での精錬が行われる場合が多く, スラグライン, メタルラインともに損傷が大きい。一方で極低炭素鋼は耐火物からのカーボンピックアップを嫌うためノンカーボン質煉瓦が使用されることが多いが, スポーリング損傷により十分な耐用が得られないことがある。本項では極低炭素鋼溶製に用いられる煉瓦に関し耐用と溶鋼の汚染抑制を両立させた製品群を紹介する。

2. 1. 1 鋼浴部用不焼成 Al_2O_3 - MgO 質煉瓦

ALTIMA (アルティマ)

ALTIMAは不定形耐火物である Al_2O_3 - MgO 質キャストブルの思想を基に開発された定形煉瓦である。キャストブル施工で必要となるミキサや型枠は不要であり, 主にステンレスメーカーの取鍋メタルライン及び敷材で使用されている。以下にALTIMAシリーズの特徴を示す。

- ・ 受熱時のスピネル生成反応により組織が緻密化し, 高い耐食性と耐浸潤性を示す。
- ・ カーボンを含有していないため溶鋼へのカーボ

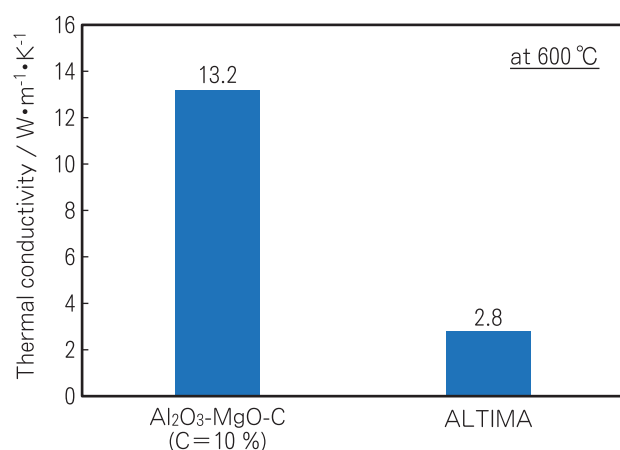


Fig. 1 Thermal conductivity of ladle bricks.

the purpose of temperature compensation and component adjustment. In practice, the equipment to be used, the type of steel to be casted, and the operation requirements are different respectively, therefore, the needs for bricks are diverse.

In this paper, ladles for ultra low carbon steel making in which carbon pick-up should be avoided, ladles for general secondary refining such as LF and RH, and ladles which require special attentions for environment such as heat loss and odor, are taken up as typical examples and the lineup of ladle bricks with recommended applications in various ladles is introduced.

2. Lineup of Bricks for Refining Ladles

2. 1 Ladle for making ultra low carbon steel

In many ladles for manufacturing ultra low carbon steel, steel refining is performed at a high temperature. Thus, both the slag line and metal zone are severely damaged. With respect to the refractory material, carbon-free magnesia-chrome refractories are often used in making ultra low carbon steels in terms of prevention of carbon pick-up from refractories. However, their durability is assumed to be insufficient due to their poor spalling resistance. In this section, suitable products for smelting ultra low carbon steel, which can achieve sufficient durability with carbon pick-up suppression, are introduced.

2. 1. 1 Unburned Al_2O_3 - MgO brick for metal zone “ALTIMA”

ALTIMA is a brick developed on the basis of the idea of Al_2O_3 - MgO castable that exhibits excellent performance. Thus, it is the product designed for steel mills that does not have castable-installation equipment such as mixer and mold. Main applications of ALTIMA are the metal zone and bottom of the steel ladle

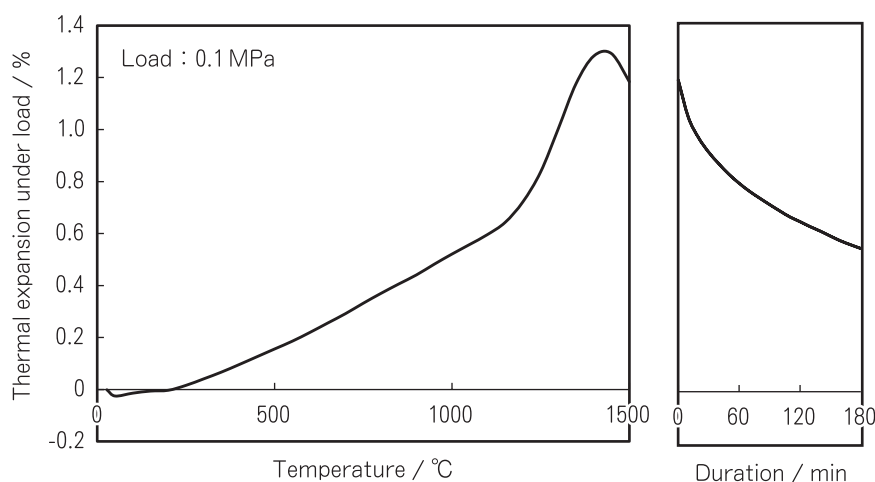


Fig. 2 Thermal expansion under load of ALTIMA.

Table 1 Typical properties of ALTIMA

	Conventional type	High corrosion resistance type
Chemical composition / mass%		
Al ₂ O ₃	88	88
MgO	7	7
After 1500 °C - 10 hours		
Apparent porosity / %	21.4	18.1
Bulk density / g·cm ⁻³	2.94	3.04
Cold crushing strength / MPa	18	20

ンピックアップを起こさず、Al₂O₃-MgO-C質などのカーボン含有系煉瓦と比べて熱伝導率が低い。熱伝導率測定結果の一例をFig.1に示す。また補修材との接着性もよく、高い補修効果が期待できる。

- ・適度な残存膨張性とクリープ特性を有しており、目地開きや迫割れを起こしにくい。また炉内面が融着し一体化するため煉瓦の脱落や目地からの地金差しが発生しにくい。Fig.2に荷重下での膨張挙動を示す。

Table 1に代表的な製品の品質値を示す。近年、高い耐食性と耐スポーリング性を有する組織を強化した高耐食性タイプが開発され、重処理操業下で高耐用を示している^{1,2)}。高耐食性ALTIMAは粒度構成の適正化により、従来ALTIMAと比較して低気孔率、高かさ比重で緻密な組織を有し、耐食性は従来材と比較し約35%向上している (Fig.3)。

of stainless steel manufacturers. Features of the ALTIMA series can be summarized as follows.

- ・ Excellent in infiltration resistance as well as corrosion resistance. It is attributed to a dense structure resulted from 'in-situ' spinel formation during heating.
- ・ Carbon-free composition. It eliminates carbon pick-up to molten steel. In addition, considerably lower thermal conductivity compared to carbon containing bricks such as Al₂O₃-MgO-C is achievable as shown in Fig.1. Furthermore, carbon-excluding composition enables firm adhesion to the repair material such as gunning and troweling, thus, service life prolongation by utilizing suitable repair is possible.
- ・ Appropriate permanent liner changes and creep deformation abilities. Thanks to carefully adjusted these properties, it prevent joint openings as well as spalling caused by thermal expansion of itself. In addition, adequate creep deformation allows to form monolithic structure at hot face side according to the fusion bonding, which is formed by mutual diffusion of small fraction of liquid phase in microstructure. Therefore, steel penetration

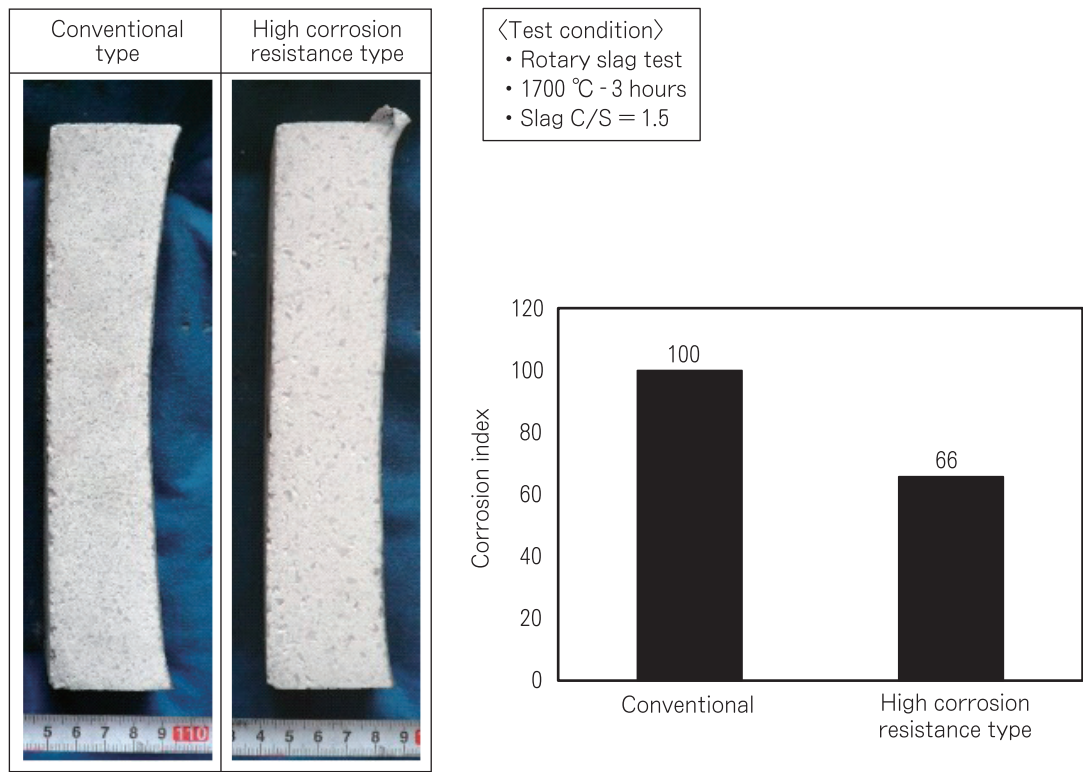


Fig. 3 Corrosion test result of ALTIMA.

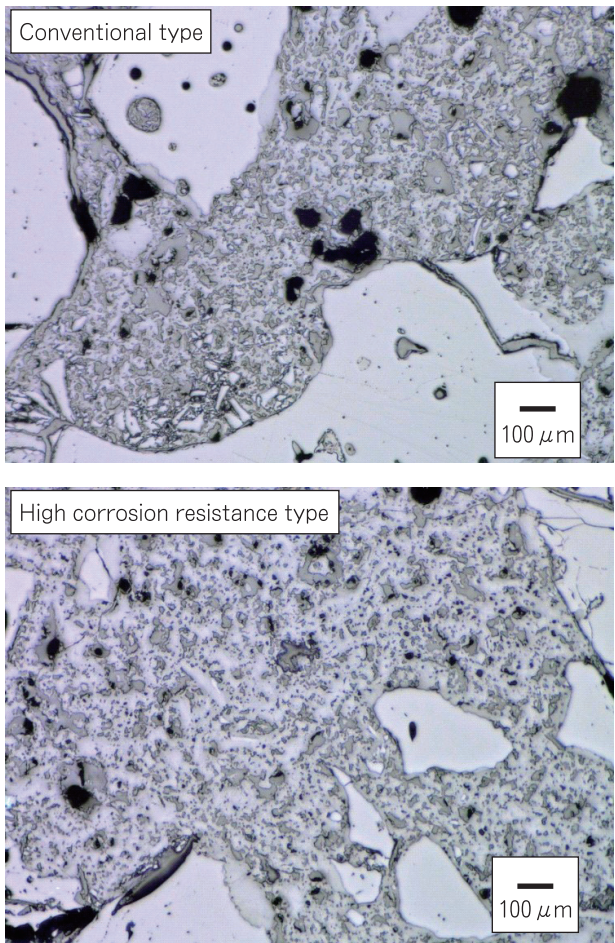


Fig. 4 Microstructures of samples after heating at 1500 °C - 10 hours.

through joints and falling out of bricks can be drastically reduced. Figure 2 shows the expansion behavior under load.

Typical properties of ALTIMA series are shown in Table 1. In recent years, high corrosion resistance type ALTIMA, which has an improved microstructure, has been developed with high corrosion and spalling resistance. Improved one has shown excellent durability in severe conditions^{1,2)}. High corrosion resistance ALTIMA has low porosity, high bulk density, and a dense structure compared with conventional ALTIMA through the optimization of grain size distribution. Therefore, the corrosion resistance is improved by approximately 35 % as compared with the conventional one (Fig. 3). The observation results of microstructure after heat treatment are shown in Fig. 4. In the post heating microstructure of high corrosion resistance type, a well-developed spinel network is observed compared with conventional one.

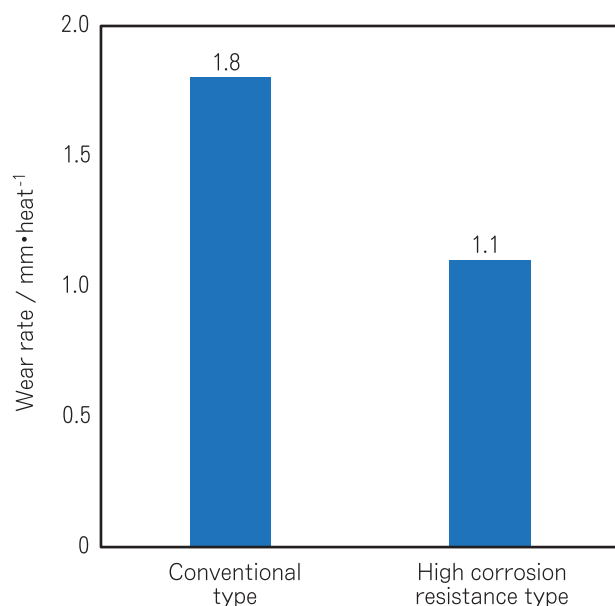


Fig. 5 Wear rate of ALTIMA.

熱処理後の微構造観察結果をFig.4に示す。高耐食性ALTIMAはマトリックス部の網目状のスピネルが従来材より太く発達している状態が観察される。電気炉メーカーA社の取鍋メタルラインで激食部に高耐食性ALTIMA、非激食部に従来材を部分張りテストしたところ、損傷速度は高耐食性ALTIMAが約40%低減されており高耐用を示した (Fig.5)。また、テスト後に回収した使用後サンプルの切断面写真をFig.6に示す。高耐食性ALTIMAはスラグ浸潤厚みが薄く、耐構造スポーリング性に優れる。

2. 1. 2 スラグライン用極低カーボン質MgO-C煉瓦

極低炭素鋼を精錬する取鍋では、耐火物からのカーボンピックアップを低減するためマグクロ煉瓦等のノンカーボン質塩基性煉瓦が使用されるケースが多い。しかしノンカーボン質塩基性煉瓦はスラグ浸潤が大きく、構造スポーリングによる損傷が問題となる。そこで当社では必要最小限のカーボンを添加し、耐スラグ浸潤性を付与した極低カーボン質MgO-C煉瓦をラインナップしている³⁾。極低カーボン質MgO-C煉瓦の特徴を以下に示す。

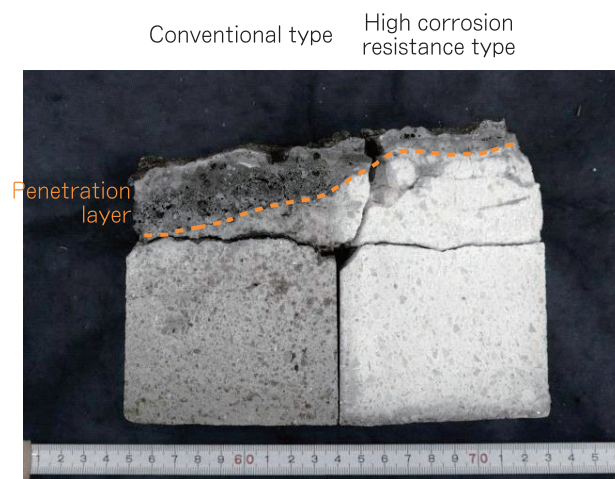


Fig. 6 Cut section of used bricks.

High corrosion resistance type ALTIMA was tested at the metal zone in an actual ladle of electric arc furnace steel manufacturer A. As a result, the wear rate of the metal zone was improved by approximately 40 %. Figure 6 shows the cut section of samples after use. High corrosion resistance type ALTIMA showed a thinner slag penetration layer and excellent structural spalling resistance.

2. 1. 2 Ultra low carbon MgO-C brick for slag line

Carbon-free basic bricks, such as magnesia-chrome bricks, are often used in the ladles for refining ultra low carbon steels in order to reduce carbon pick-up from refractories. Carbon-free basic bricks, however, causes slag penetration to form thick slag penetration layer, resulting in severe structural spalling. Therefore, we have a lineup of ultra low carbon MgO-C bricks containing the minimum necessary carbon in order to prevent slag penetration³⁾. The characteristics of ultra low carbon MgO-C brick are shown below.

- Minimum amount of graphite. It is obtained by intensifying the dispersibility of the graphite. The well-dispersed graphite structure renders excellent slag penetration resistance

・黒鉛の分散性を高めることで黒鉛の添加量を最小限に抑えている。また、分散した黒鉛の働きで優れた耐スラグ浸潤性を有し、かつMgO同士の焼結を抑制できるため耐スポーリング性が高い。

and can suppress over-sintering of MgO with each other. Hence, the high spalling resistance is achieved.

・ Low post-heating porosity. It improves the corrosion resistance.

Table 2 Typical properties of ultra low carbon MgO-C brick

	Conventional type	High corrosion resistance type (C=1.5 %)	High corrosion resistance type (C=5 %)
Chemical composition / mass% MgO C	95 1.5	95 1.5	92 5
After drying Apparent porosity / % Bulk density / g•cm ⁻³ Cold crushing strength / MPa	6.8 3.10 78	5.3 3.15 64	3.9 3.21 50
After 1500 °C - 3 hours Apparent porosity / %	9.1	7.8	6.6
Thermal spalling resistance index	180	160	100

	Ultra low carbon MgO-C brick (C = 5 %)	Direct bonded MgO-Chrome brick	〈Test condition〉 • Rotary slag test • 1700 °C - 5 hours • Slag C/S = 2.5
Cross-section			
Corrosion Index	100	103	
Slag penetration depth / mm	0	32	

Fig. 7 Corrosion test result of MgO-C brick and MgO-Chrome brick.

- ・粒度構成の適正化により熱処理後気孔率を低減させることで耐食性を高めている。

Table 2に代表的な製品の品質値を示す。Fig.7に耐食性試験を実施した極低カーボン質MgO-C煉瓦とマグクロ煉瓦の試験結果を示す。スラグに対する耐食性は同等だが、マグクロ煉瓦は厚いスラグ浸潤層が形成されている。一方で極低カーボン質MgO-C煉瓦はスラグ浸潤が見られず、スラグ浸潤に伴う構造スポーリングに対して強いと言える。極低カーボン質MgO-C煉瓦はカーボンピックアップも少なく安定使用できる点から極低炭素鋼製造用取鍋のスラグライン材に適している。

近年開発された高耐食性タイプの極低カーボン質MgO-C煉瓦は更に組織を緻密化し耐食性を改善した材質である。Fig.8に取鍋スラグラインで使用

The typical properties of the products are shown in Table 2. Figure 7 shows the corrosion test results of ultra low carbon MgO-C bricks and magnesia-chrome bricks. Although the corrosion resistance is comparable, the magnesia-chrome brick has a thick slag penetration layer. On the other hand, slag penetration is not observed in the ultra low carbon MgO-C bricks. The ultra low carbon MgO-C bricks, therefore, are resistant to the structural spalling accompanying slag penetration. Hence, it can be concluded that ultra low carbon MgO-C bricks are suitable for use at the slag line of ladles for producing ultra low carbon steels. Stable performance with little carbon pickup is promising.

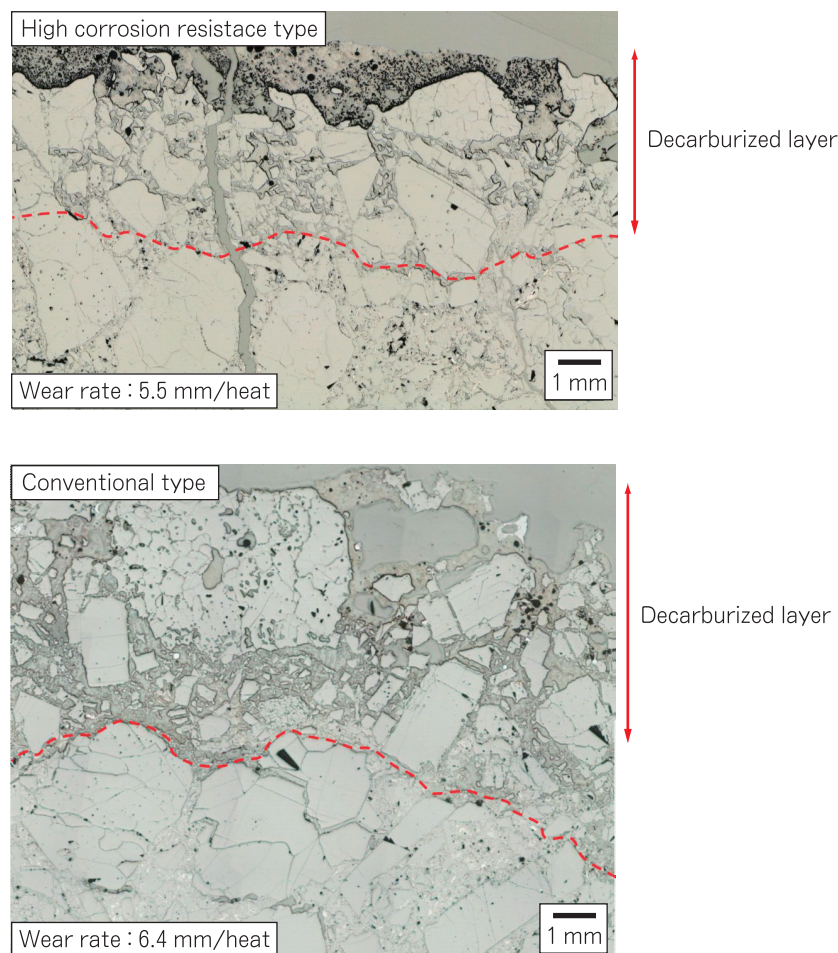


Fig. 8 Microstructure of ultra low carbon MgO-C near the hot face after use.

された使用後稼働面の微構造写真を示す。両タイプともに稼働面に脱炭層が認められるが、従来タイプと比較して高耐食性タイプは脱炭層厚みが薄い。また高耐食性タイプの脱炭後組織は緻密であり稼働面の煉瓦組織が溶出しにくく、高耐食性を示すものとする。

2. 2 LFやRHなどの一般的な二次精錬を行う取鍋

二次精錬の普及とともに取鍋ワーク耐火物の高耐用化が図られた結果、現在では二次精錬用取鍋のワーク耐火物はMgO-C質やAl₂O₃-MgO-C質に代表されるカーボン含有系耐火物が広く使用されている。取鍋のワーク耐火物のうちスラグラインと敷湯あたりはとりわけ損傷が大きく、ネックになりやすい部位である。本項ではこれらの部位で高耐用を示す製品群を紹介する。

2. 2. 1 スラグライン用高充填MgO-C質煉瓦HIDEN（ハイデン）

取鍋スラグラインの損傷はスラグ溶損が主体であり、特にポーラスプラグ等による攪拌の影響を受ける部位では耐火物の溶損が大きくなる。こうした激食部には高耐食性材質の適用が不可欠である。当社では繰り返し加熱による組織脆化に着目し⁴⁾、耐食性に優れる高充填MgO-C煉瓦HIDENを

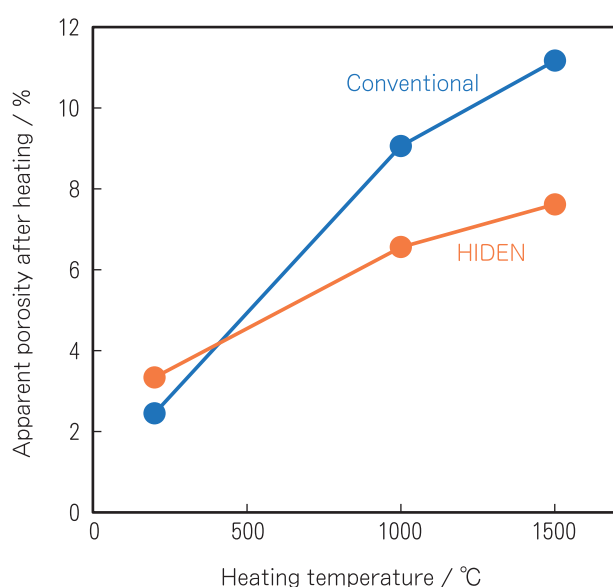


Fig. 9 Comparison of apparent porosity of HIDEN and conventional MgO-C brick as a function of heating temperature.

The recently developed high corrosion resistant ultra low carbon MgO-C bricks have a denser structure, resulting in further improvement of corrosion resistance. Figure 8 shows micrographs near the hot face of bricks used in the ladle slag line. The high corrosion resistance type showed thinner decarburized layer and denser microstructure after decarburization. It indicates that the high corrosion resistance type material exhibits excellent erosion resistance even if it is decarburized.

2. 2 Ladles for general secondary refining such as LF and RH

For several decades, ladle bricks have been improved continuously along with an increase in secondary refining. As a result, carbon containing bricks such as MgO-C and Al₂O₃-MgO-C are widely used as working refractories for secondary refining ladles at present. Among the working refractories, slag line bricks and impact zone bricks tend to be severely damaged. Therefore, improving the performance of these bricks is crucial. This section introduces products with high durability at these positions.

2. 2. 1 High density MgO-C bricks for slag lines “HIDEN”

It is well-known that the dominant factor that limits service life of steel ladle slag line bricks is erosion at the region affected by stirring by the gas purged from plug refractories such as porous plug and slit plug. Thus, it is necessary to apply high corrosion resistance material to such a severe wear zone. We focused on microstructure deterioration due to repeated heating⁴⁾, and developed HIDEN, a high density MgO-C brick with excellent corrosion resistance⁵⁾ The characteristics of HIDEN are shown below.

- Excellent corrosion resistance through suppressed structure deterioration. Figure 9 compares the post-heating porosity of

Table 3 Typical properties of HIDEN and conventional MgO-C brick

	Conventional type	HIDEN
Chemical composition / mass% MgO C	83 11	83 11
After drying Apparent porosity / % Bulk density / g·cm ⁻³ Cold crushing strength / MPa	3.0 3.05 40	2.9 3.12 38
After 1500 °C - 3 hours Apparent porosity / %	9.7	7.9

開発した⁵⁾。HIDENの特徴を以下に示す。

- ・ 熱処理後気孔率を低減し、組織脆化を抑制することで極めて高い耐食性を有する。一例としてFig.9に一般的なMgO-C煉瓦とHIDENの熱処理後気孔率を示す。
- ・ カーボン量によらずHIDENテクノロジーは適用可能であり、スラグ組成に応じて適切なカーボン量のHIDENを選択可能である。

Table 3に代表的な製品の品質値を示す。また侵食試験結果をFig.10に示す。従来材と比較してHIDENは1500℃熱処理後の見掛け気孔率が低く、侵食試験において約30%損傷が小さい。Fig.11に従来材質とHIDENの実炉におけるパネルテスト後の煉瓦切断面を示す。両者のマグネシアや黒鉛のグレードに違いはないが、HIDENは約35%損傷が小さい結果であった。

2. 2. 3 取鍋敷湯当たり部用高充填

Al₂O₃-MgO-C質煉瓦

取鍋において敷はメタルラインと並び安定した耐用が求められる部位であるため、剥離や目地開きを起こしにくいAl₂O₃-MgO-C煉瓦が使用されることが多い。敷湯当たり部の損傷要因としては、煉瓦同士のせり割れによる稼働面剥離、残存膨張不足による目地開きや出鋼時に底に溜まったスラグによる溶損が考えられてきた。しかし特に湯当たり部の損傷が大きいケースにおいて溶鋼がマトリックス部に侵入したような組織を示すこと

conventional MgO-C and HIDEN. Lower porosity after heating is the evidence of structure deterioration suppression.

- ・ Wide applicability of HIDEN technology. It is applicable regardless of the amount of carbon and an appropriate amount of carbon can be selected according to slag compositions.

The typical qualities of products and the result of the corrosion test are shown in Table 3 and Fig. 10, respectively. Compared with the conventional material, HIDEN has a low apparent porosity after heat treatment at 1500 °C and showed approximately 30 % less damage in the corrosion test. Figure 11 shows the cut sections of the conventional material and HIDEN after panel test in an actual ladle. Although there is no difference in the purity of magnesia and graphite between HIDEN and conventional one, HIDEN exhibited approximately 35 % less damage.

2. 2. 3 High density Al₂O₃-MgO-C brick for impact zone

Since the bottom, as well as metal zone, of the steel ladle is an important portion requiring stable durability, Al₂O₃-MgO-C bricks, which are very resistant to peeling or joint opening, are often used. Causes of damage to the impact zone are thought to include peeling of the hot face due to cracking, joint opening due to insufficient residual expansion and corrosion by slag. In cases where impact zone damage is severe, the matrix structure can be seen to be penetrated with molten steel (Fig. 12). This is presumably because the molten steel discharged from the converter or the electric arc furnace penetrated the brick structure due to the impact of falling. Figure 13 shows the microstructure of the steel penetration portion. Hardly any graphite can be observed in the steel penetration layer. On the other hand, the precipitation of fine carbon was confirmed in the penetrated steel. From

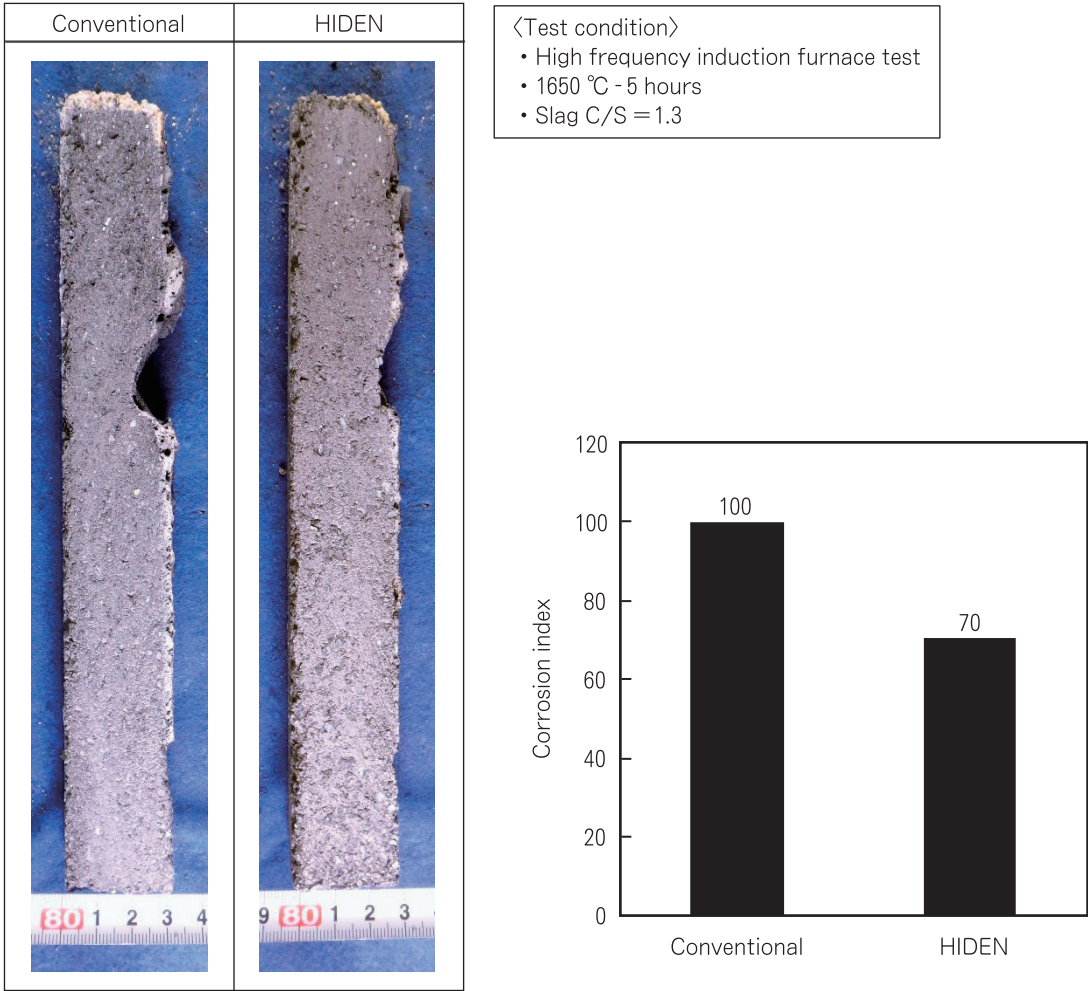


Fig. 10 Corrosion test result of MgO-C bricks.



Fig. 11 Cut section of used conventional MgO-C and HIDEN.

がある (Fig.12)。これは転炉や電気炉から排出された溶鋼が落下する際の衝撃により煉瓦組織内に侵入したためと考えられる。Fig.13に地金侵入部の微組織写真を示す。地金侵入層には黒鉛はほと

these results, it is assumed that the molten steel dissolved graphite in the brick during operation, and penetrated through pores generated by the disappearance of graphite. As a result



Fig. 12 Cut section of bricks used in impact zone of steel ladle.

Table 4 Typical properties of Al_2O_3 -MgO-C for impact zone

	Conventional type	High density type
Chemical composition / mass%		
Al_2O_3	62	75
MgO	20	8
C	11	8
After drying		
Apparent porosity / %	4.8	3.8
Bulk density/ $\text{g}\cdot\text{cm}^{-3}$	3.25	3.33
Cold crushing strength / MPa	45	40
After 1500 °C - 3 hours		
Apparent porosity / %	11.2	9.7

んど残存していない。一方で侵入した地金を拡大すると微細な炭素の析出が確認される。このことから稼働中に溶鋼が煉瓦内の黒鉛を溶解し、黒鉛の消失によって生成した気孔を介して侵入に至ったと推定される。このような損傷に対し種々検討を重ねた結果、耐用性に優れる取鍋湯当たり用高充填 Al_2O_3 -MgO-C煉瓦を開発した。特徴を以下に示す。

- ・耐スポーリング性と耐溶鋼侵入性のバランスに優れる。
- ・敷湯当たり用高充填 Al_2O_3 -MgO-C煉瓦は従来品に比べ低気孔率で気孔径も小さく、煉瓦組織内への溶鋼侵入に強い。

Table 4に従来材と高充填品の標準品質表を示す。高充填品は化学組成や粒度構成等の最適化により、1500℃-3h還元熱処理後気孔率が約15%

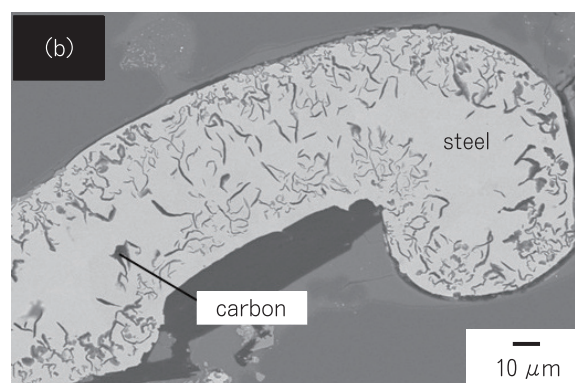
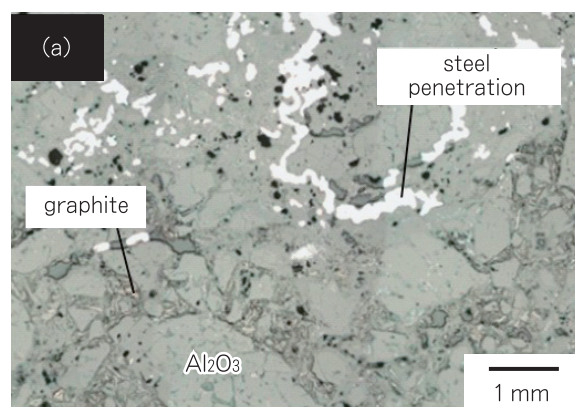


Fig. 13 Microstructure of (a) molten steel penetration zone in used brick and (b) precipitated carbon in penetrated steel.

of various investigations on such damages, high density Al_2O_3 -MgO-C brick with excellent in durability was developed. The features are shown below.

- ・ The well-balanced spalling resistance and steel penetration resistance.
- ・ Lower porosity and small pore size. These favorable features of high density Al_2O_3 -MgO-C bricks provides sufficient resistant to steel penetration particularly at the impact zone where suffers from considerable steel falling impact.

Table 4 shows the typical properties of conventional materials and high density Al_2O_3 -MgO-C. As for the post-heating porosity under a reducing atmosphere, high density Al_2O_3 -MgO-C is approximately 15 % smaller

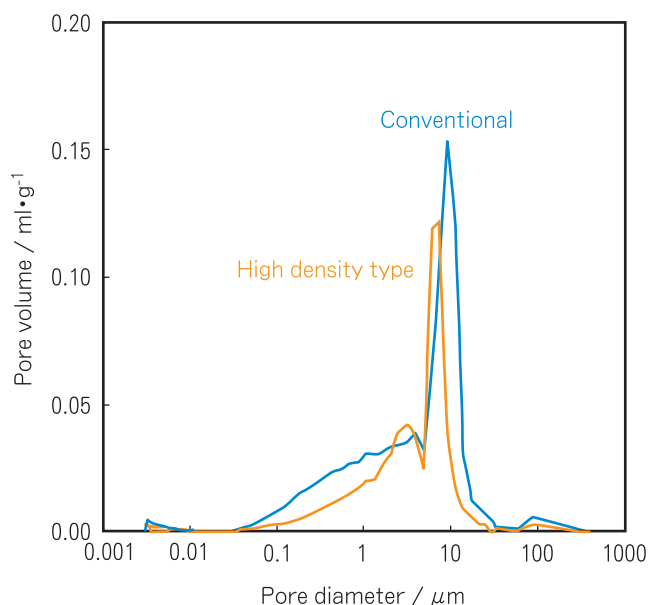


Fig. 14 Pore size distribution of $\text{Al}_2\text{O}_3\text{-MgO-C}$ bricks after heat treatment at 1500°C in a reducing atmosphere and decarburization at 800°C in an oxidizing atmosphere.

低減している。Fig.14に黒鉛溶解・消失後の組織を想定した 1500°C -3h還元熱処理後に 800°C -48h脱炭した試料の気孔径分布を示す。高充填 $\text{Al}_2\text{O}_3\text{-MgO-C}$ 煉瓦の気孔径はピークが微細な方向にシフトしており、最頻値が $9\mu\text{m}$ から $6\mu\text{m}$ に縮小した。

Fig.15にFig.12と同じ電気炉メーカーで使用した高充填品湯当たり煉瓦の切断面写真を示す。溶鋼の侵入は軽微で改善の効果が認められる。またFig.16に各電気炉メーカーでの従来材と高充填品の使用結果を示す。多数の電気炉メーカーにおいて高充填 $\text{Al}_2\text{O}_3\text{-MgO-C}$ 煉瓦は従来品より損傷速度が低減された。

2. 3 臭気、熱ロスに配慮が必要な取鍋

二次精錬を実施する取鍋用煉瓦には耐食性や耐スポーリング性の観点から、カーボン含有系耐火物が広く使用されているが、これらの耐火物は熱伝導率が高く鉄皮からの熱ロス増大や鉄皮の変形等の問題が発生する。また不焼成のカーボン含有系煉瓦は乾燥・予熱時に臭気や発煙が発生するため、作業環境面から改善を要望されることがある。

than conventional material by optimization of chemical composition and grain size distribution.

Figure 14 shows the pore size distributions of $\text{Al}_2\text{O}_3\text{-MgO-C}$ bricks after the double heat treatment of which the samples were heated at 1500°C for 3 hours in a reducing atmosphere followed by decarburization at 800°C for 48 hours in an oxidizing atmosphere. The double heat treatment was performed to simulate the microstructure just before steel penetration, i.e., decarburized structure of pre-sintered material. The pore diameters of the high density $\text{Al}_2\text{O}_3\text{-MgO-C}$ bricks were shifted to fine peaks, and the mode diameter was reduced from $9\mu\text{m}$ to $6\mu\text{m}$.

Figure 15 shows cut sections of high density $\text{Al}_2\text{O}_3\text{-MgO-C}$ bricks used in the same steel manufacturer as Fig.12. The penetration of molten steel is minor compared with conventional material. Figure 16 shows the application results of conventional and high density $\text{Al}_2\text{O}_3\text{-MgO-C}$ bricks used in the impact zone of steel ladles at various steel mills. In many steel mills, the wear rates of high density $\text{Al}_2\text{O}_3\text{-MgO-C}$ bricks were improved compared with conventional materials.

2. 3 Ladles that require countermeasures for odors and heat loss

Carbon containing refractories are widely used in ladle bricks for secondary refining from the viewpoints of corrosion resistance and spalling resistance. However, these materials have disadvantages according to their high thermal conductivity such as increased heat loss from the shell and shell deformation. In addition, odor and smoke, which are emitted from unburned carbon containing bricks, are required to be suppressed in terms of the working environment.

On the other hand, in transfer ladles in which



Fig. 15 Cut section of high density $\text{Al}_2\text{O}_3\text{-MgO-C}$ bricks used in impact zone of steel ladle.

一方、二次精錬を実施しない搬送用取鍋では古くからろう石煉瓦がスラグライン、メタルライン共に使用されている。一般に搬送用取鍋はLF等の二次精錬を行わず温度補償ができない。そのため軽量で熱伝導率が低いろう石煉瓦は搬送用取鍋に適しているが、近年ろう石煉瓦は供給面で問題があり、ろう石煉瓦に代わる材料のニーズが高い。

本項ではこれらの用途に合わせた熱ロスや臭気・発煙に配慮した製品を紹介する。

2. 3. 1 二次精錬用環境対応型カーボン含有煉瓦 ECONOS (エコノス)

ECONOSは低熱伝導性と低臭気の特徴とするカーボン含有系定形煉瓦であり、二次精錬を実施する多くの取鍋用煉瓦で採用されている。ECONOSシリーズの特徴を以下に示す。

- ・ECONOSテクノロジーはカーボン含有系煉瓦であれば材質を問わず同様の効果が得られる。
- ・同一カーボン含有量の煉瓦と比べ、耐用を損なうことなく熱伝導率を約30%低減できる。 MgO-C および $\text{Al}_2\text{O}_3\text{-MgO-C}$ 煉瓦の例として従来材質とECONOSの熱伝導率をFig.17に示す。
- ・フェノール樹脂を使用していないため、乾燥予熱時の臭気発生が抑制でき有害ガスの発生量も

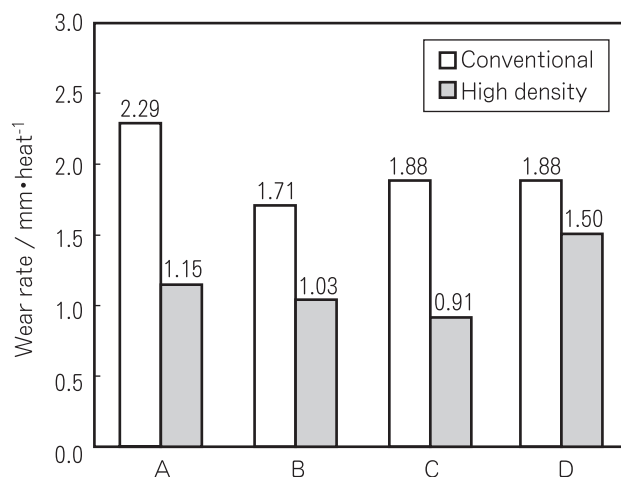


Fig. 16 Comparison of wear rate between conventional and high density $\text{Al}_2\text{O}_3\text{-MgO-C}$ bricks used in impact zone of steel ladle at various steel mills.

secondary refining is not performed, pyrophyllite bricks have long been used for both the slag line and metal zone. In general, the transfer ladle does not perform secondary refining such as LF, hence, no temperature compensation by utilizing metallurgical reaction is expected. Therefore, pyrophyllite bricks with light weight and low thermal conductivity are suitable for transfer ladles. Since it is fired brick, no emissions of odor and smoke occurs. In recent years, however, tight supply of pyrophyllite bricks became serious issue. Thus, demand for alternatives is increasing. This section introduces products that shows low heat loss, odor and smoke according to these applications.

2. 3. 1 Environmentally friendly carbon-containing refractories for secondary refining ECONOS

ECONOS is a carbon containing brick characterized by low thermal conductivity and low fumes. Therefore, ECONOS have been used in many steel ladles for secondary refining. Characteristics of the ECONOS series are shown below.

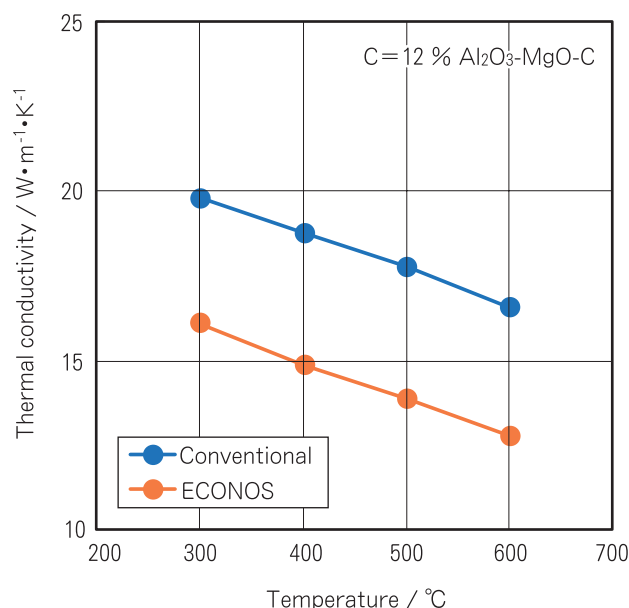
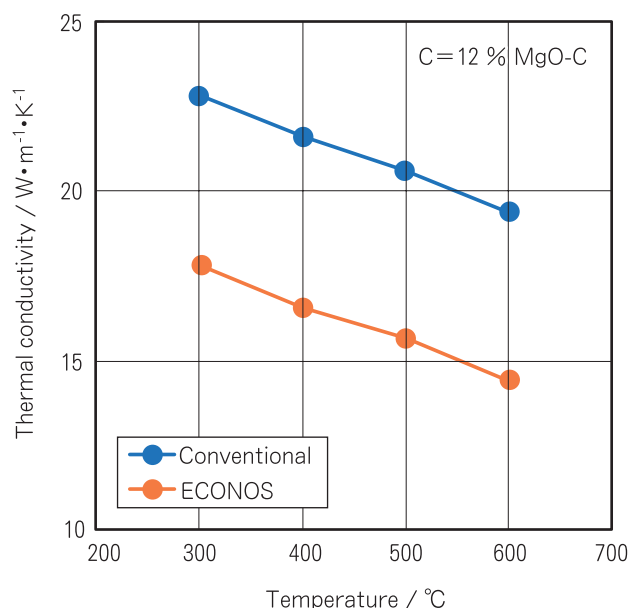


Fig. 17 Thermal conductivity of MgO-C and Al₂O₃-MgO-C bricks.

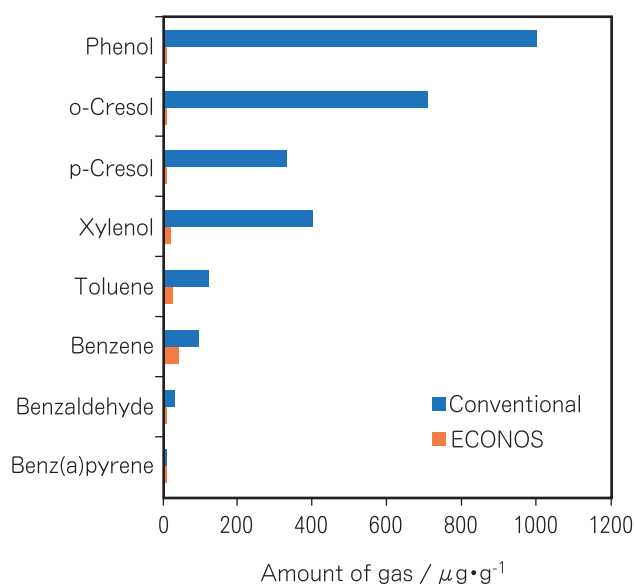


Fig. 18 Amount of gas components generated from MgO-C bricks during heat-up.

少ない。従来材質とECONOSの加熱時に発生する芳香族ガスの測定結果をFig.18に示す。

- ・カーボン含有系煉瓦の耐用上のネックとなる目地損傷やラットホールを起こしにくい。

Table 5に各材質の標準品質表を示す。取鍋用煉瓦としてはスラグラインにMgO-C質, メタルライン, 敷にAl₂O₃-MgO-C質が適用されることが多

- ・ Low thermal conductivity with equivalent Graphite content. ECONOS has about 30 % lower thermal conductivity than conventional material with the equivalent carbon content. Figure 17 exemplifies the thermal conductivity of MgO-C and Al₂O₃-MgO-C bricks with and without ECONOS technology.
- ・ A tiny fraction of emissive matters. Thanks to the state-of-the-art phenol resin-excluding binder system, the generation of undesirable odor and toxic gas during drying and pre-heating is suppressed. Figure 18 compares the measurement results of the aromatic gas generated during heating of the conventional material and ECONOS.
- ・ Stable durability. It is unlikely to cause joint erosion and rat holes that tends to affect the durability of carbon containing bricks.
- ・ Wide applicability. The ECONOS technology is applicable to any kinds of carbon containing brick regardless of the material.

Table 5 shows the typical properties for the respective materials. As a ladle brick, MgO-C

Table 5 Typical properties of ECONOS

	ECONOS	
Material	MgO-C	Al ₂ O ₃ -MgO-C
Chemical composition / mass%		
MgO	83	10
Al ₂ O ₃		71
C	11	10
After drying		
Apparent porosity / %	3.4	5.0
Bulk density / g・cm ⁻³	3.11	3.23
Cold crushing strength / MPa	32	35

い。実機における鉄皮温度測定結果をFig.19に示す。ECONOSを使用した鍋は明らかに鉄皮温度が低く、鉄皮からの放熱が抑制されている。

2. 3. 2 軽量・低熱伝導性搬送取鍋用Al₂O₃-C質煉瓦

前記したようにろう石煉瓦は軽量で低熱伝導性であり、温度補償のできない搬送用取鍋に適した材料である。ろう石煉瓦は日本国内での生産が縮小しつつあり、中国からの輸入が増加している。しかし近年、中国において環境規制や品位の低下によりろう石原料の採掘が難しくなっている。さらにじん肺による作業者の健康問題で生産から撤退するメーカーが増加しており、安定供給ができない状態になりつつある。そこで当社ではろう石煉瓦の代替として新規搬送用取鍋煉瓦を開発した。特徴を以下に示す。

material is for the slag line and Al₂O₃-MgO-C material is for both the metal zone and bottom.

Figure 19 shows the shell temperature distribution of the actual ladle measured during commercial operation. The ladle of ECONOS lining has a markedly low shell temperature, which means the heat radiation from the shell is suppressed considerably.

2. 3. 2 Light weight and low thermal conductivity Al₂O₃-C brick for transport ladle

As described above, lightweight, low thermal conductivity pyrophyllite brick is suitable option for transportation ladles in which re-heating of molten steel cannot be expected. While, the production of pyrophyllite bricks in Japan is gradually decreasing. Instead, imports from China are increasing. However, in recent years, it has become difficult to mine pyrophyllite raw materials due to environmental regulations and deterioration of quality in China. Moreover, the number of manufacturers withdrawing from production due to the health problem of workers caused by pneumoconiosis is increasing. Hence, a stable supply is becoming difficult. Thus, for molten steel transporting ladles, we have developed a new ladle brick as a substitute

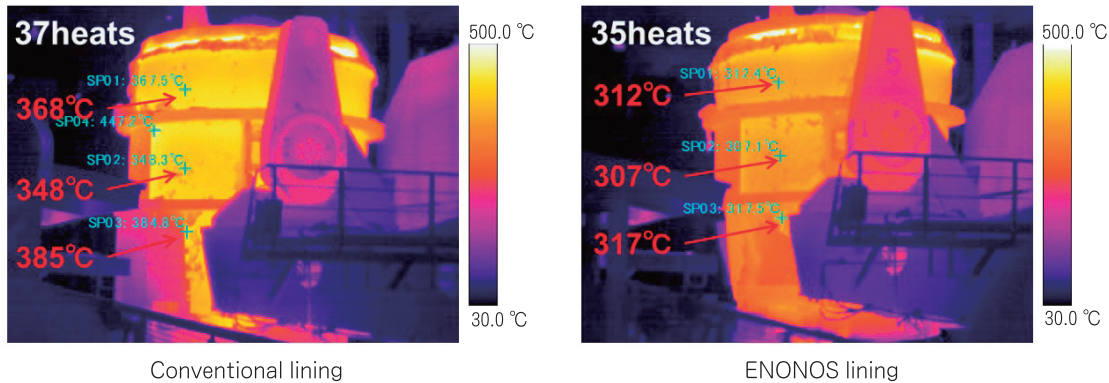


Fig. 19 Comparison of shell temperatures between conventional and ECONOS lining.

- ・ろう石煉瓦よりはやや重いが、その他一般的な取鍋煉瓦と比べ大幅に軽量である。標準品質表をTable 6に示す。ろう石煉瓦と比較して、開発品A、Bともにかさ比重はやや高い値を示すが、取鍋ワーク材として使用される高アルミナ質や Al_2O_3 -MgO-C質と比べ大幅に軽量である。
- ・乾燥・予熱時に臭気を発しない
- ・ろう石煉瓦と比べ、高い耐食性を示す。また耐スポーリング性にも優れる。一例として高周波誘導炉を用いた侵食試験結果をFig.20に示す。

for pyrophyllite brick. Features of the developed brick are shown below.

- ・ Light weight. While it is slightly heavier than pyrophyllite bricks, it is much lighter than other conventional ladle bricks. Typical qualities of the developed brick are shown in the Table 6. Although both developed bricks A and B have slightly higher bulk density compared with traditional pyrophyllite brick, they are significantly lighter than high alumina and Al_2O_3 -MgO-C bricks used as

Table 6 Typical properties of pyrophyllite and developed material A and B

	Pyrophyllite	Developed material A	Developed material B	High Alumina	Al_2O_3 -MgO-C
Chemical composition / mass%					
SiO ₂	84	34	53	11	20
MgO		61	43	85	62
Al ₂ O ₃	14	3	3		11
C					
After drying					
Apparent porosity / %	13.2	11.7	12.5	18.9	4.8
Bulk density / g・cm ⁻³	2.29	2.72	2.48	2.85	3.25
Fume generation during heat up	Fume-less	Fume-less	Fume-less	Fume-less	Severe fume

	Pyrophyllite	Developed material A	Developed material B	<Test condition> ・ High frequency induction furnace test ・ 1600 °C - 2 hours ・ Slag C/S = 0.6
Cross-section				
Corrosion index				
Slag line	100	58	83	
Metal zone	100	26	28	

Fig. 20 Corrosion test result of pyrophyllite and developed material A and B.

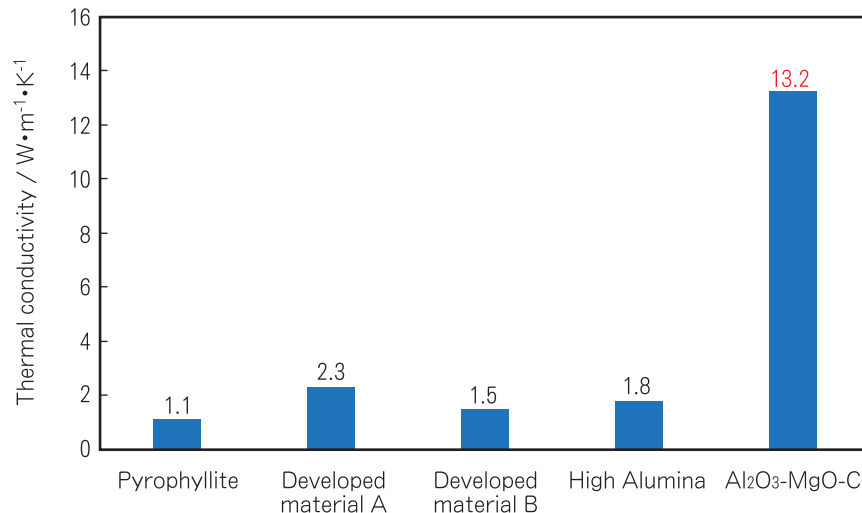


Fig. 21 Thermal conductivity of ladle bricks.

開発品の耐食性はいずれも良好で、特に鋼浴部はろう石煉瓦と比べて約70%高い耐食性を示す。

Fig.21に各材質の熱伝導率を示す。開発品はカーボン含有系煉瓦であるが熱伝導率はAl₂O₃-MgO-C煉瓦より大幅に低く、ろう石煉瓦に近い値をしめす。取鍋側壁を想定したライニングでの定常伝熱計算結果をFig.22に示す。開発品はAl₂O₃-MgO-C煉瓦と比較して、鉄皮温度は約100℃低い値を示し、ろう石ライニングとほぼ同等の結果であった。これらの点から開発品はろう石煉瓦の代替材質として良好な耐用が期待される。

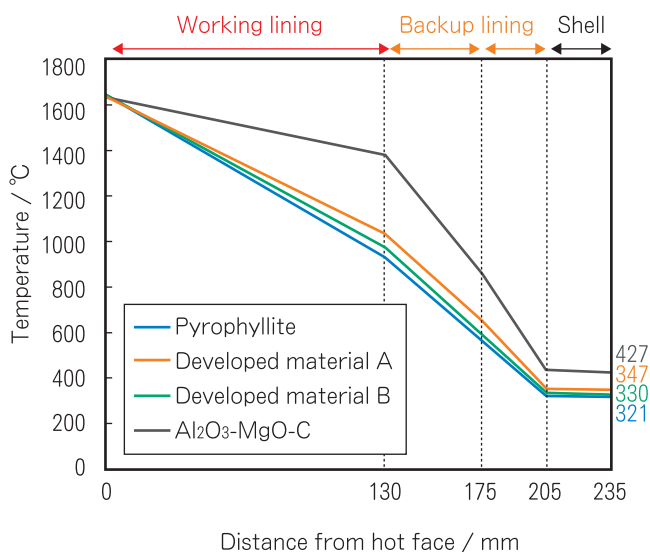


Fig. 22 Results of steady heat transfer calculation.

work linings of the ladle.

- No odor during drying and preheating
- Superior durability. The developed bricks exhibits higher corrosion resistance than pyrophyllite brick as well as excellent spalling resistance. The results of the corrosion test using a high frequency induction furnace are shown in Fig. 20. The corrosion resistance of each developed brick is good, and in particular, the corrosion resistance of the developed bricks in the metal zone is approximately 70 % higher than that of the pyrophyllite brick.

Figure 21 compares the thermal conductivity of each material. Despite the developed bricks contain graphite, their thermal conductivities are much lower than those of the Al₂O₃-MgO-C brick, which is close to that of the pyrophyllite brick. Figure 22 shows the steady-state heat transfer calculation results for the refractory lining simulating ladle side wall. The developed bricks showed lower shell temperatures of approximately 100 °C compared with Al₂O₃-MgO-C bricks and the results were almost equivalent to those of a pyrophyllite brick lining. From these points, the developed bricks are expected to show good durability as a substitute material for pyrophyllite brick.

3. おわりに

取鍋用煉瓦は用途によって様々な特性を要望されるため、用途に適した材質を選定する必要がある。当社の取鍋用煉瓦製品は種々の特性を備えており、適切な材質を選定することで顧客の抱える問題の解決ができると考える。今後とも特徴ある材質の開発を進めていく。

3. Epilogue

Since ladle bricks are required to have various characteristics depending on the application, it is necessary to select a material suitable for the application. From our wide variation in ladle brick line-up, optimal materials for individual industrial demand can be selected. We will continuously address to develop unique materials.

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