

SHINAGAWA TECHNICAL REPORT

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組織強化による高耐食性化

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Improving Microstructure

土 井 菜保子
Naoko DOI

飯 田 敦 久
Atsuhisa IIDA

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品川技報

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土 井 菜 保 子^{*1}
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飯 田 敦 久^{*2}
Atsuhisa IIDA

富 谷 尚 士^{*3}
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要 旨

溶鋼鍋用不焼成 Al_2O_3 - MgO れんが“ALTIMA”の耐スラグ侵食性向上について検討した。結果、ALTIMAの耐スラグ侵食性には受熱後のスピネル形成反応に伴う組織形成が重要な役割を果たすこと、また、組織形成には原料の粒度分布と成形体の充填構造が影響することが判明した。検討結果を基に開発した高耐用品の実炉テストにおいても良好な結果が得られている。

Abstract

The corrosion resistance of unburned Al_2O_3 - MgO bricks was improved by focusing on the in-situ microstructure evolution associated with the spinel forming reaction. A suitable microstructure evolution was achieved by densification of a green body consisting of raw materials with an appropriate grain size distribution. The effectiveness of the improved materials was validated by a laboratory corrosion test as well as commercial application to a steel ladle metal line.

1. はじめに

近年、鉄鋼各社において高品位の鋼を得るために溶鋼処理の重処理化が進み、それに伴い溶鋼鍋のメタルライン部において従来使用されてきた高アルミナれんがでは耐用的に満足の得られないケースが増加している。またカーボン含有系耐火物をメタルライン部に適用している場合には、れんが中のカーボンの溶鋼中への溶解（カーボンピックアップ）やれんが自体が高熱伝導であるために熱ロスや鉄皮の変形が問題となる場合がある。

上記の問題に対応する製品として、カーボンを含まない不焼成 Al_2O_3 - MgO れんがALTIMAが

1. Introduction

Recently, the load on refractories for the steel ladle has been increasing in accordance with the increase in secondary refining treatment. Therefore, improvement in the durability of the refractories is required not only for the slag line but also for the metal line of steel ladles. Burned high Al_2O_3 bricks, which are widely used in the steel ladle metal line lining, show insufficient durability due to poor corrosion resistance. While unburned Al_2O_3 - MgO -C bricks, which are also commonly used for steel ladle refractories, show better corrosion and

*1 技術研究所 第1研究部 理学博士 Dr. Sci., Research Dept. No.1, Research Center.

*2 技術研究所 第1研究部 第1研究室 室長 General Manager, Shaped Refractories R&D Sec., Research Dept. No.1, Research Center

*3 西日本工場 岡山製造部 係長 Assistant Manager, Technical Sec., Okayama Plant, West Japan Works

ある。ALTIMAは日本国内の銑鋼一貫製鉄所の溶鋼鍋で汎用的に使用されている Al_2O_3 - MgO 質キャストブルと同等の特性を有するれんがとして開発された。その特徴の詳細については過去に報告されている¹⁾⁻⁴⁾が、簡潔にまとめると以下の様になる。

- 1) カーボンを含んでいないため低熱伝導率であり、カーボンピックアップも起こさない。
- 2) 不焼成であるため、Fig.1に示す様に Al_2O_3 - MgO 質キャストブルと同様、稼働時にスピネル生成反応を生じ結合組織を強化しつつ体積膨張する。
- 3) 上記の反応に伴い、目地開きが抑制されることに加え、拘束下におけるクリープ変形により組織強化が促進された結果、耐食性・耐スラグ浸潤性が向上する。
- 4) 従来のれんがと同様の施工が可能であり、ミキサーや型枠、乾燥用設備等の不定形施工設備を必要としないため初期導入コストが不要である。

一方で、近年の重処理化に伴い更なる高耐用化が求められている。今回はALTIMAの耐スラグ侵食性（耐食性）に着目して改良した結果、大幅な耐用向上が認められたので実炉使用結果と合せて報告する。

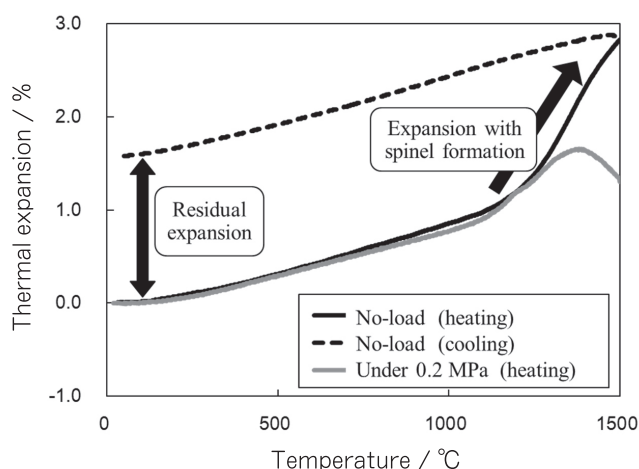


Fig.1 Thermal expansion behavior of conventional type ALTIMA.

thermal shock resistance, they have negative influences such as carbon pick up into molten steel and/or excessive heat emission.

In order to deal with these issues, we previously developed ALTIMA, an unburned Al_2O_3 - MgO brick, for the metal line lining. The original idea in developing ALTIMA came from Al_2O_3 - MgO castables, which are popular materials for the steel ladle metal line exhibiting sufficient performance in the Japanese integrated steel mills. The favorable features of ALTIMA¹⁾⁻⁴⁾ are briefly summarized as follows;

- 1) Carbon free composition allows low thermal conductivity, which prevents heat loss, as well as eliminating the risk of carbon pick up.
- 2) An unburned structure enables in-situ spinel formation that strengthens the bonding structure along with increasing volume as shown in Fig.1, resulting in the prevention of joint openings.
- 3) Thanks to appropriate creep deformation (also shown in Fig.1), further structure strengthening, which improves corrosion and penetration resistance, is achieved by heating under restrained conditions.
- 4) Extra investments for castable refractory installation equipment such as mixers, molds, vibrating facilities and drying facilities are unnecessary.

Though ALTIMA has many favorable features, modern intensive steel refining treatment requires further improvement in the corrosion resistance of this brick. In this paper, our new findings on the slag corrosion resistance of ALTIMA, i.e., influence of in-situ microstructural development on the slag corrosion resistance, and test results of newly developed ALTIMA in a commercially operated steel ladle are described.

2. ALTIMAの組織強化と耐食性

2. 1 背景

一般に、れんがの耐食性には原料の種類や配合割合、気孔率、結合組織など、様々な要因が影響を与える。中でも、実炉使用時のスピネル生成反応を特徴とするALTIMAにおいては、受熱後に形成される組織が重要な役割を果たす可能性が高い。受熱後の組織は充填構造の影響を受けると考えられることから、粒度構成適正化による充填構造強化が受熱後の結合組織ならびに耐食性に与える効果について検討した。

2. 2 実験

従来のALTIMA（以下、従来品と表記）に加え、試行錯誤的に粒度構成を変更した結果、充填構造の強化が確認された2種類の試作品A、Bを用意した。従来品、試作品共にアルミナを88質量%、マグネシアを7質量%用いており化学組成は一定であるが、各使用原料の最大粒径や粒度の配合割合を変更している。これら3試料の膨張挙動を測定し、スピネル生成挙動を比較した。更に結合組織を評価するため、大気雰囲気下で1500℃-10時間熱処理したサンプルの組織観察および気孔径分布測定を行った。また、耐食性はアーク加熱式回転ドラム法で評価した。試験は1650℃で5時間実施し、一時間ごとに塩基度2.0の合成スラグを入れ替えた。

2. 3 実験結果

従来品を100とした場合の成形後のかさ密度および、1500℃-10時間熱処理後の諸特性をTable 1

2. Influence of Microstructure Evolution on Corrosion Resistance of ALTIMA

2. 1 Background

Generally, many factors such as the chemical composition, kinds of raw materials, porosity, microstructure, and so on, influence the corrosion resistance of refractories. Among those factors, we empirically assumed that the in-situ microstructure evolution associated with the spinel forming reaction is essential for the improvement of the corrosion resistance of ALTIMA. Based on that assumption, optimum packing structure that suitably promotes in-situ microstructure evolution and consequential improvement in slag corrosion resistance was investigated.

2. 2 Experimental methods

In order to validate that assumption, the following three samples; conventional type ALTIMA and two types of densely-packed trial samples (A and B) were prepared. The chemical compositions of each sample were identically 88mass% alumina and 7mass% magnesia. For the two trial samples, the maximum grain size and grain size distribution were adjusted by trial and error method to maximize the green packing degree. Subsequent to mixing the raw materials with a binder addition, the mixtures were pressed followed by curing in an electric oven.

For evaluations of the microstructure evolution associated with the spinel forming reaction, measurements of apparent porosity, pore diameter distribution, and also microstructure observations by EPMA were carried out for each sample after heating at 1500℃ for 10h in an electric furnace.

In addition, the high temperature thermal expansion behavior of each sample was measured since the spinel forming reaction is

Table 1 Properties of test samples

	Conventional type	Sample A	Sample B
Chemical composition (mass%)			
Al ₂ O ₃	88	88	88
MgO	7	7	7
Green packing degree	100.0	103.6	103.0
After 1500℃-10h			
Apparent porosity (%)	21.4	18.1	17.0
Bulk density (g•cm ³)	2.94	3.04	3.04
Modulus of rupture (MPa)	18	20	21

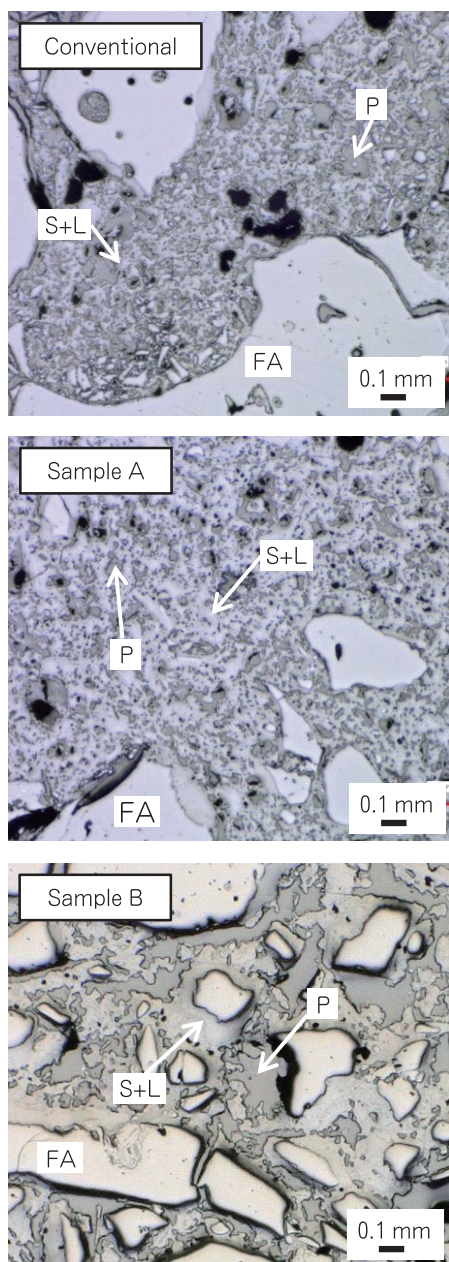


Fig.2 Microstructures of samples after heating at 1500°C-10h. FA, fused alumina; S+L, fine spinel and liquid; P, pore.

に示す。試作品A、Bともに従来品よりも成形後かさ密度が約3%増加し、粒度構成変更による充填強化に成功した。また、1500°C-10時間熱処理後も従来品より低気孔率、高かさ比重であった。また、曲げ強度は試作品がやや大きい値を示した。

一方で、試作品A、Bの受熱後組織は大きく異なっていた。Fig.2は1500°C-10時間熱処理後の微組織写真である。試作品Aのマトリックスは細か

accompanied by considerable volume increase.

The slag corrosion resistance of these samples was evaluated by rotary drum method utilizing an electric-arc as the heat source. The test was performed for 3 hours at 1650°C using slag with a basicity of 2.0. The slag was exchanged every 1 hour so as to maintain corrosivity.

2. 3 Experimental results

The green packing degree, which is normalized by conventional type, and properties after heating at 1500°C for 10 hours are listed in Table 1. The green packing degree of both trial samples A and B were approximately 3% larger than that of the conventional type. The smaller apparent porosity and larger bulk density of the post heated samples also indicate that the densely-packed structure of trial samples was retained after high temperature heat treatment. The post heating modulus of rupture of the trial samples was slightly larger than that of the conventional type.

On the other hand, the post heating microstructures were markedly different among these three samples. Fig.2 shows the microstructure of each sample after heating at 1500°C for 10h. In each specimen, fused-alumina grains and a network texture consisting of very fine spinel particles and liquid phase were observed. Hereafter, the network texture is referred to as spinel network. The microstructure of sample A is very similar to the conventional one, however, the degree of spinel network development is much higher. On the other hand, sample B showed a matrix with poorer spinel network development (Fig.2).

While the pore diameter of trial sample A was distributed in almost same range as the conventional type, as shown in Fig.3a, trial sample B showed a larger pore diameter distribution as is obvious in Fig.3b.

As shown in Fig.4, the thermal expansion

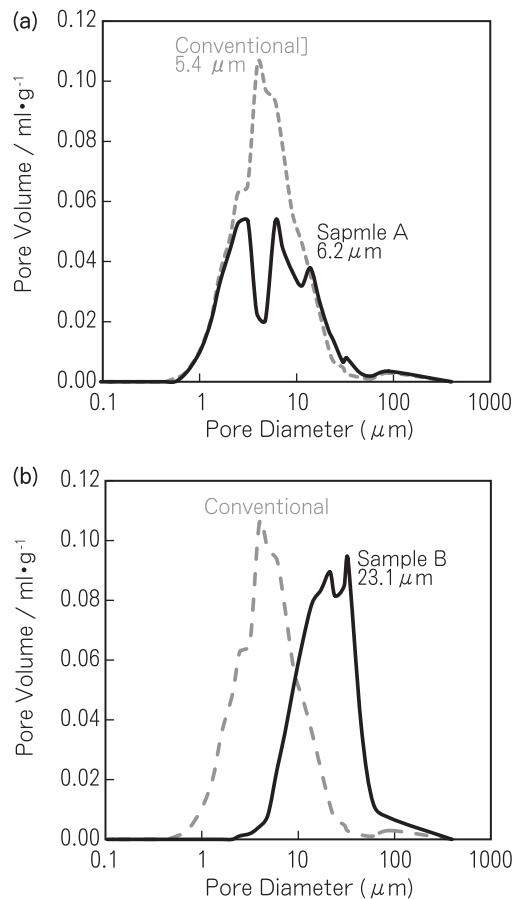


Fig.3 Pore size distribution after 1500°C-10h. The values of median pore diameter of each sample are also indicated in the figures.

い網目状に発達したスピネルと液相から成るネットワーク組織により構成され、従来品と良く似た様相を示すがスピネルの結合はより太く発達していた。一方で、試作品Bは従来品と比較してスピネルの結合組織が細かく発達していなかった (Fig.2)。また、試作品Aの気孔径は従来品と同様の分布範囲を示した (Fig.3a) が、試作品Bは径が増大する方向にシフトしていた (Fig.3b)。

Fig.4に各試料の無荷重下における熱膨張率測定結果を示す。試作品Aは従来品と同様約1150°Cからスピネル生成反応に伴う膨張が検出され、1500°Cにおける膨張量は若干大きかった。また、試作品Bでは約1250°Cと従来品より約100°C高い温度からスピネル生成反応に伴う膨張が検出されたが、1500°Cにおける膨張量は同程度であった。

耐食性に関しても、試作品A, Bで大きく異なる

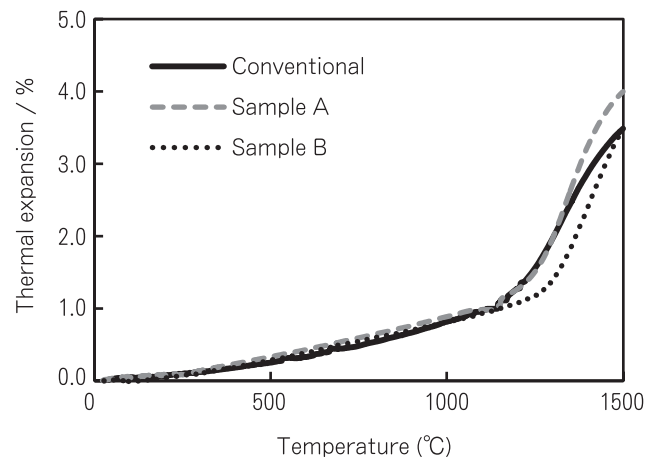


Fig.4 Comparison of thermal expansion behavior among each sample.

behavior of each sample varied as well. While rapid expansion induced by spinel formation was detected from 1150°C both for conventional material and trial sample A, trial sample A showed larger thermal expansion at 1500°C. The beginning point of the rapid expansion of trial sample B was detected at 1250°C, which was higher than the conventional material and trial sample A, however, the thermal expansion of trial sample B at 1500°C is almost identical to conventional material.

The corrosion resistance of the samples also varied. Figs. 5 and 6 show cross-section of the samples after the corrosion test and the corrosion index of the samples, respectively. While almost no improvement in the corrosion resistance was recognized for densely-packed trial sample B, trial sample A demonstrated a 35% reduction in corrosion. In each post corrosion tested sample, only a shallow slag penetration layer, i.e., 1-2mm in thickness, was observed.

2. 4 Discussion

In this subsection, the microstructure evolution process at high temperature is discussed followed by a description of the influence of the microstructure on corrosion resistance.



Fig.5 Cross-section of samples after corrosion test.

結果となった。Fig.5に侵食試験後サンプルの切断面写真を、Fig.6に従来品の侵食量を100とした場合の侵食指数を示す。従来品とほぼ同様の侵食量を示した試作品Bに対し、試作品Aは大幅に侵食量が少なく、耐食性にして約35%向上した。また、いずれの試料もスラグ浸潤深さは1-2mm程度であった。

2. 4 考察

試作品A、Bはともに従来品に対して低気孔率、高密度化が図られており、かつそれらの値が同程度であったにも関わらず、受熱後の組織および耐食性は大幅に異なっていた。これらの結果は、粒度構成による充填構造の差が受熱後組織を決定し、更には耐食性に影響することを示唆している。そこで、充填構造が受熱後組織に与える影響と、受熱後組織と耐食性の関係について以下に考察した。

全ての試料においてマトリックスに少量の液相が観察された (Fig.2) ことから、受熱後組織、即ち網目状に発達したスピネルの結合組織は、陽イオンの液相を介した拡散に伴い形成された可能性

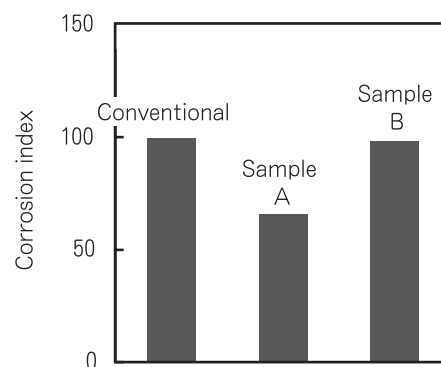


Fig.6 Corrosion index of each sample.

Although the post heating apparent porosity and bulk density of both trial samples were almost same, the post heating microstructures which are evaluated by degree of spinel network development, were varied. These results suggest that the post heating microstructures, i.e., spinel network development degree, depends on the grain size distribution and packing structure of the green body.

Under the high temperature condition, spinel (MgAl_2O_4) is formed by the in-situ reaction between Al_2O_3 and MgO . Thus, in the case of unburned Al_2O_3 - MgO material, “microstructure evolution” is equivalent to spinel network development. Existence of a small amount of liquid phase in the spinel network of all samples (Fig.2) indicates that the dominant mechanism of spinel formation at high temperature was cation diffusion in the liquid. Therefore, the proximal arrangement of Al_2O_3 and MgO grains would result in a thick layer of the development of the spinel network. Since the contact point of these grains become the junction of the spinel network, detailed development of the spinel network can be achieved by increasing the density of the contact points.

These two effects, i.e., proximity and contact

が高い。ともに、成形後の Al_2O_3 と MgO 粒子間の距離が近いほど結合組織が太く発達し、接点が多いほど細かい網目状になると考えられる。

上記の考えに基づくと、試作品Aと従来品の受熱後組織の差は、成形後かさ密度増大により粒子間の距離が近接した効果をより反映していると考えられる。試作品Aの 1500°C における熱膨張率の増加 (Fig.4) も、同じ理由で説明することができる。一方で、試作品Bと従来品の受熱後組織の違いは、成形後かさ密度増大よりも、 Al_2O_3 と MgO 粒子の接点が少ない効果をより反映していると考えられる。接点の減少は反応速度を低下させる要因となるため、試作品Bにおいてスピネル生成反応に伴う膨張開始温度がより高温で検出された結果とも整合的である (Fig.4)。

次に耐食性について考察する。れんが成分のスラグ中への拡散過程が溶損速度を律速していると仮定すると、試作品Aの耐食性向上は、受熱後の結合組織強化および気孔率減少に由来するスラグとの接触面積の減少により説明することができる。一方で、試作品Aと同程度の気孔率かつ大きな気孔径を有する試作品Bでは、スラグとの接触面積は大幅に減少するものの耐食性は大幅に劣る結果から、他の要因が溶損を律速していることになる。

試作品Bの低耐食性は、気孔径の増大に伴い気孔内に侵入したスラグとバルクスラグとの交換が促進された結果である可能性がある。物質の拡散を記述するFickの法則より物質流速 J は以下の式(1)で示され、れんがの溶解速度は飽和濃度に近づくほど減少することになる。

$$J = \frac{D}{\delta} (n_s - n) \dots\dots\dots (1)$$

ここで D 、 δ 、 n_s および n はそれぞれ、拡散係数 (m^2/s)、境界層の厚み (m)、飽和濃度 (kg/m^3) および液相濃度 (kg/m^3) である。気孔径の大幅な増加は、気孔内に侵入したスラグの流動抵抗を低下させ、バルクスラグとの交換を容易にする。結果、気孔内に侵入したスラグ中に溶けだした耐火物成分は飽和濃度に達し難くなり、溶損が促進されたと考えられる (Fig.7)。

point density, can explain the difference in the microstructures after heating. The high development degree of spinel network in densely-packed trial sample A is considered attributable to the proximal arrangement of unreacted alumina and magnesia grains achieved by the densification of the green body. On the other hand, the low development degree of spinel network in spite of low porosity in the trial sample B reflects the lower density of the contact points of grains, which is attributable to grain size arrangement. It is consistent with the results for thermal expansion behavior in Fig.4, that is, promotion of spinel formation in trial sample A resulted in higher expansion, and, the inhibition of spinel formation in trial sample B raised the detected point of rapid expansion beginning temperature.

Next, the influence of the microstructure on slag corrosion resistance will be discussed. Assuming that mass transfer limits refractory dissolution, largeness in contact area between refractory structure and molten slag is one of the most important factors influencing corrosion resistance to slag. Hence, improvement of the corrosion resistance in trial sample A can be explained by reduction of the contact area derived from the complex well-developed spinel network structure and smaller apparent porosity after heating. However, it is impossible to explain the poor corrosion resistance of the trial sample B by this mechanism since a smaller contact area would be achieved for low porosity and large pore size sample B. Thus, it was suspected that another factor governs the corrosion mechanism of trial sample B.

The poor corrosion resistance of trial sample B is considered attributable to the large pore diameter as shown in Fig.2. In this structure, it is easy to exchange the infiltrated slag with bulk slag due to low flow resistance, resulting

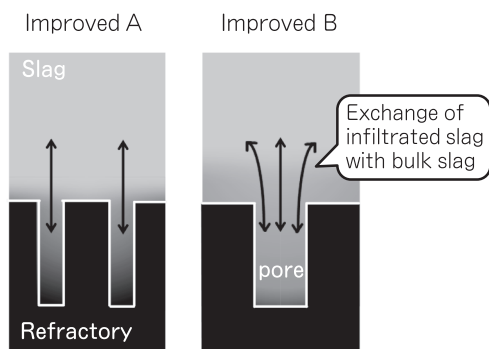


Fig.7 Image of interaction between slag and samples.

3. 実炉使用結果

以上の知見をもとに開発したALTIMA改良品のメタルライン部分張りテストを電気炉メーカーA社の溶鋼鍋にて行った。円周方向の最激食部位に施工された改良品と、非激食部に施工された従来品の損傷速度を比較するとそれぞれ1.1および

in a low saturation degree of the slag infiltrated refractory. According to Fick's Law, which describes the diffusion process, mass flux J ($\text{kg/m}^2\text{s}$) can be expressed by Eq. (1).

$$J = \frac{D}{\delta} (n_s - n) \cdots \cdots \cdots (1)$$

Where, D , δ , n_s and n denote the diffusion coefficient (m^2/s), effective boundary layer thickness (m), saturation concentration (kg/m^3) and concentration (kg/m^3), respectively. As indicated in Eq. (1), the refractory dissolution rate becomes higher as the saturation degree of refractories components in molten slag decreases. Since it is natural to hypothesize that the refractory composition dissolves in infiltrated slag as well as bulk slag, a higher dissolution rate in the infiltrated slag promotes overall refractory corrosion (Fig.7).

Thus, our empirical assumption that the microstructure evolution is essential for the improvement of the corrosion resistance of ALTIMA was experimentally validated.

3. Results of Field Trial

We developed a new ALTIMA brick based on the results described above, and the developed ALTIMA was used for the metal line lining in a commercially operated actual steel ladle at an electric furnace steel-maker. As a result, marked improvement in the wear rate was recognized as follows; 1.1mm/heat for developed material installed for corrosive zone and 1.8mm/heat for conventional one installed for the ordinal zone (Fig.8).

As is obvious in the cross sections of the bricks after use, in Fig.9, the newly developed ALTIMA exhibited thinner slag penetration layer thickness. Hence, excellences in structural spalling resistance as well as slag corrosion resistance were verified by commercial application.

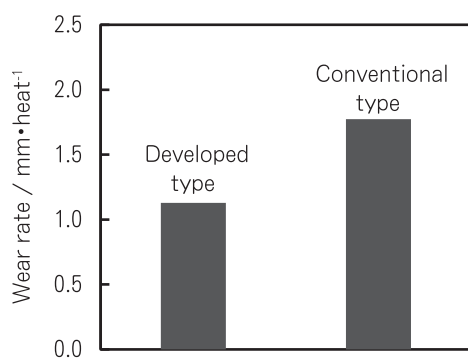


Fig.8 Wear rate of bricks.

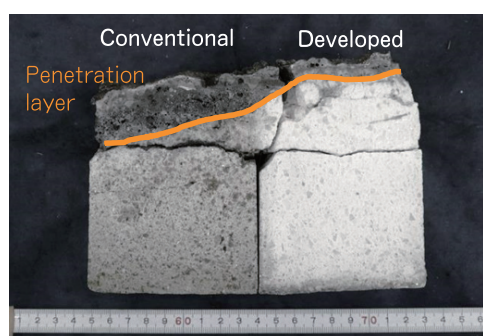


Fig.9 Cross-section of used bricks.

1.8mm/chであり、大幅な耐用向上が認められた (Fig.8)。また、テスト後に回収した使用後サンプルの切断面をFig.9に示す。改良品はスラグ浸潤厚みが薄く、耐構造スポーリング性にも優れることが示された。

4. まとめ

溶鋼鍋メタルライン用不焼成 Al_2O_3 - MgO れんが“ALTIMA”の耐スラグ侵食性に着目し、高耐用化を検討した。耐スラグ侵食性には受熱後の気孔率のみならず、スピネル形成反応に伴う組織形成が重要な役割を果たすことが判明した。開発品を用いた実炉試験結果でも良好な結果が得られている。

4. Conclusion

We developed unburned Al_2O_3 - MgO bricks with high corrosion resistance for steel ladles. The developed brick was obtained according to the investigation results that the in-situ microstructural development associated with the spinel forming reaction at high temperature is important for improvement of corrosion resistance. The developed bricks showed excellent durability at the metal-line in a commercially operated steel ladle.

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