

SHINAGAWA TECHNICAL REPORT

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島 田 岳

Gaku SHIMADA

飯 田 敦 久

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柿 原 昌 佳

Masayoshi KAKIHARA

古 谷 彰 平

Shohei FURUYA

品川技報



品川リフラクトリーズ株式会社
SHINAGAWA REFRACTORIES CO.,LTD.

報文 REPORT

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島 田 岳 ^{*1}	飯 田 敦 久 ^{*2}
Gaku SHIMADA	Atsuhisa IIDA
柿 原 昌 佳 ^{*3}	古 谷 彰 平 ^{*4}
Masayoshi KAKIHARA	Shohei FURUYA

要 旨

本報では、MgOの粒度構成が組織脆化に及ぼす影響を明らかにするために1.0mm以下のMgOを篩い分けし、粒度構成を変化させた試料を作製し、評価を行った。MgOの表面積が増加するに従い、重量減少率が大きくなり反応に伴う組織脆化が認められた。一方で、通気率が同程度の試料であれば表面積の大きい試料の方が重量減少率は増加しており、表面積はMgO-C反応に影響していることが明らかとなった。また、れんが組織脆化には、れんが系外へガスが拡散する際の抵抗性が大きく影響しており、これらには、6 μ m以上の大きな気孔の増加が最も影響すると示唆された。

Abstract

In this paper, in order to clarify the effect of the grain size composition of MgO on microstructure deterioration, MgO of 1.0 mm or less was screened to prepare samples in which the grain size compositions were changed, and the evaluation was carried out. As the surface area of MgO increased, the weight reduction rate increased, and deterioration of the microstructure was observed accompanied by a reaction. On the other hand, when the permeability was about the same, the weight reduction rate of the samples having a large surface area increased, and it was revealed that the MgO-C reaction had a direct effect on the surface area. It was also suggested that resistance to diffusion of gas out of the brick greatly influenced the healthiness of the brick structure, and the increase in large pores of 6 μ m or more had influence.

1. 緒言

MgO-Cれんがは、主骨材として高融点かつ高塩基度スラグに対し優れた耐食性を持つマグネシ

1. Introduction

The MgO-C brick is a refractory material obtained by combining magnesia, which has a

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

*2 技術研究所 第1研究部長 General Manager, Research Dept. No.1, Research Center

*3 技術研究所 第1研究部 第1研究室 主任研究員 Staff Manager, Shaped Refractories R&D Sec., Research Dept. No.1, Research Center

*4 名古屋営業所 第4営業部 Sales Dept. No.4, Nagoya Sales Office

アとスラグに対して濡れ難く、高い熱伝導率、低熱膨張率を有する黒鉛を組み合わせた耐火物である。また、精錬用耐火物として広く使用されており、例として転炉、電気炉等の内張りレンガ、炉底に用いる羽口レンガ、溶湯の出湯口用レンガ等がある。

近年当社のMgO-Cレンガは、組織制御技術により改良を進めてきた経緯がある¹⁾。MgO-Cレンガの損傷要因としては、溶損や酸化、割れなどがあり、特に転炉直胴部に使われるMgO-Cレンガの損傷は溶損が中心であり、原料純度のみならず組織脆化抑制の観点を重視した開発が進められてきた。

Fig.1に転炉直胴部にて使用された使用後MgO-Cレンガの稼働面微構造写真を示す。レンガ稼働面表層では、黒鉛と共にマトリクス部を構成する微細なMgO粒子も消失しており、組織脆化層が形成されている。この脆化層の形成については、スラグ中へのMgO溶出やスラグ中铁酸化物による黒鉛の液相酸化、更にはレンガを構成するMgO粒子と黒鉛が高温化で反応するMgO-C反応の関与が報告されており²⁻⁴⁾、また日野らは均質にMgO-C反応が進行する未反応核モデルを用いた検証を行っており、反応速度に影響の大きい因子としてMgO粒子径を挙げている⁵⁾。一方、Fig.2に

high melting point and excellent corrosion resistance to high basicity slag as a main aggregate, and graphite, which has high thermal conductivity and a low thermal expansion coefficient and is resistant to slag wetting. It's also widely used as a refractory for refining. For example, there are bricks for basic oxygen furnaces (BOF) and electric arc furnaces (EAF), tuyere bricks used for the furnace bottom, and tap hole bricks. Recently, our MgO-C products have been developed from the aspect of microstructural engineering¹⁾. The damage factors of MgO-C brick are dissolution, oxidization, and spalling. In particular, the damage of the MgO-C brick used in the barrel of the BOF is mainly due to dissolution. Development has been promoted from the viewpoint of inhibiting microstructure deterioration as well as raw material purity. A microstructure photograph of the MgO-C brick hot face used in a BOF barrel is shown in Fig. 1. In the hot face layer of the brick, the fine MgO particles, which constitute the matrix part together with the graphite, disappear, and a microstructure deterioration layer is formed. The formation of this fragile layer has been reported to involve the elution of MgO into the slag, liquid phase oxidation of graphite by iron oxide in the slag, and a MgO-C reaction in which the MgO particles and graphite composing the brick react at high temperature²⁻⁴⁾. Hino et al. conducted tests using unreacted nuclear models in which MgO-C reactions proceed homogeneously in the paper, and cited MgO-particle size as a major factor influencing the reaction rate⁵⁾. On the other hand, Fig. 2 shows that MgO-C brick, heat-treated at high temperatures, has lower corrosion resistance as the porosity increases¹⁾. As for the effect of brick porosity on the MgO-C reaction, it has

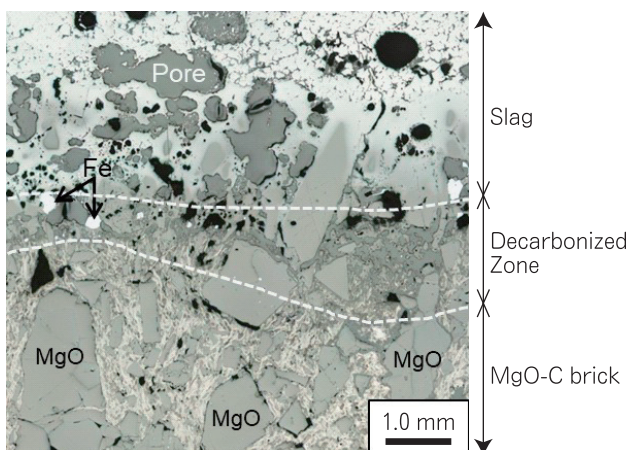


Fig. 1 Microstructure of used MgO-C brick near hot face.

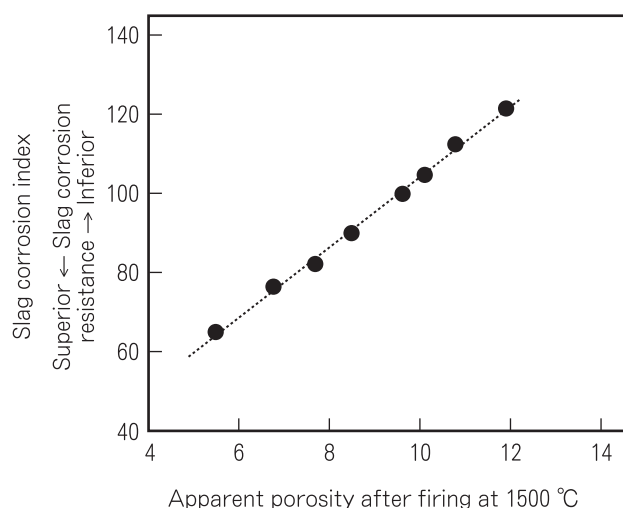


Fig. 2 Variations in slag corrosion index as a function of apparent porosity after firing at 1500 °C under reducing atmosphere.

示す様に高温熱処理を行ったMgO-Cれんがは高気孔率であるほど耐食性が低下することが実験的に確認されている¹⁾。れんがの気孔率がMgO-C反応に与える影響については、土井らがMgO-C反応は試料の表面からのMgガス、COガスの拡散により進行し、高気孔率であるほど反応速度が大きくなることが報告されており^{2,5)}、MgO-Cれんがの損耗を抑えるためには、組織の緻密化と脆化の抑制が重要となる。

そこで本報では、MgOの粒度構成が組織脆化に及ぼす影響を明らかにするためにマトリクス部を構成する1.0mm以下のMgOを篩い分けし、粒度構成を変化させた試料を作製後、MgOの表面積を変化させた場合の気孔率、通気率等を調査し、組織脆化に対するこれらの影響を検討した。

2. 実験方法

2. 1 試料作製

原料には、電融MgO、鱗片状黒鉛、各種微量添加物及びバインダーとしてフェノール樹脂を用いた。化学組成は重量比でMgO : C = 83 : 15とした。また、1.0mm以下のMgO原料をa, b, c ($a > b > c$, $1.0\text{mm} > a > b > 0.1\text{mm} > c$) の3粒度にふるい分けし、Fig.3に示すように粒度構成を

been reported by Doi et al. that the MgO-C reaction proceeds by diffusing Mg gas and CO gas from the surface of the sample, and that the reaction rate increases as the porosity increases^{2,5)}. In order to suppress the wear of MgO-C brick, densification of the structure and suppression of microstructure deterioration are essential. In this paper, in order to clarify the influence of the grain size distribution of MgO on microstructure deterioration, a sample in which the matrix was composed with a grain size distribution that was changed by screening MgO to 1.0 mm or less was produced. The brick properties such as porosity, permeability and so on were measured when the surface area of MgO was changed, and the effect of grain size composition on microstructure deterioration was investigated

2. Experiment

2. 1 Sample

MgO, flake graphite, various trace additives and phenolic resin were used as raw materials. The chemical composition was MgO : C = 83 : 15. MgO raw material of 1.0 mm or less was screened into three particle sizes of a, b, and c ($a > b > c$, $1.0\text{ mm} > a > b > 0.1\text{ mm} > c$). The difference in the particle size composition of the prepared samples is shown in Fig. 3. Numbers in parentheses indicate the surface area as an index when No. 1 is 100. The surface area index was calculated by calculating each average particle diameter of a, b, and c from the particle size distribution and calculating the surface area of particles of 1.0 mm or less of each blend based on the blending ratio. That is, it is shown that sample No. 1 has the smallest surface area and sample No. 9 has the largest surface area. All the sample preparation conditions other

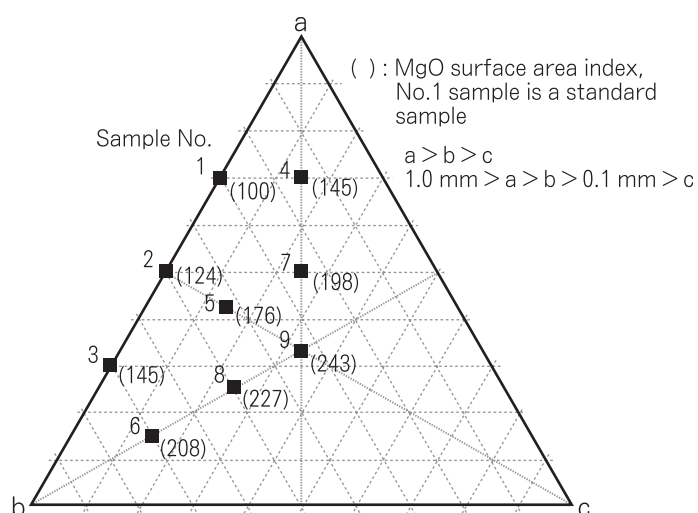


Fig. 3 Particle size constitution of MgO less than 1 mm of the sample.

変化させ、試料を作製した。括弧内の数字はNo.1を100とした時の表面積を指数化して示している。表面積指数は、a, b, cの各平均粒子径を粒度分布から見積もり、配合割合を基に各配合の1.0mm以下の粒子の表面積を算出した。No.1の試料が最も表面積が小さく（粗い粒が多く）、No.9の試料が最も表面積が大きい（微細な粒が多い）。成形条件や乾燥条件など、MgOの粒度構成以外の試料作製条件は全て統一した。

2. 2 試料の評価

・一般品質

乾燥後と1600℃焼成後の動弾性率、曲げ強度、圧縮強度、見掛け気孔率およびかさ比重の測定を行った。実機稼動時の状況を想定し焼成後の試験温度は、1600℃とした。MgO-Cレンガの試験片をグラインドソニックにより動弾性率を求めた後、曲げ試験を行った。曲げ試験は治具スパン間距離が100mmのものを使用した。また、試験後の試験片から圧縮強度とアルキメデス法により見掛け気孔率とかさ比重を測定した。

・通気率

MgO-Cレンガを加工し、コークスブリーズ中で1500℃の熱処理した後に通気率測定装置を用いて通気率を測定した。

than the particle size structure of MgO, such as molding conditions and drying conditions, were unified.

2. 2 Evaluation

・ General Property Evaluation

As general properties, the dynamic elastic modulus, modulus of rupture, crushing strength, apparent porosity, and bulk density were measured after drying and after firing at 1600 °C. The test temperature of firing was 1600 °C assuming the situation at the time of actual operation. After the dynamic elastic modulus was determined, modulus of rupture, crushing strength, apparent porosity and bulk density using Archimedes method were measured.

・ Permeability

The MgO-C bricks was processed and heat-treated at 1500 °C in a coke breeze, and then the permeability was measured using the permeability measuring device.

・ Pore Size Distribution

The pore size distributions of MgO-C bricks heat-treated at 1500 °C in a coke breeze were measured by mercury injection method.

・ MgO-C Reaction Test

The MgO-C reaction test was conducted using the atmosphere-controllable furnace shown in Fig. 4. Furthermore, the weight reduction rate obtained in the MgO-C reaction test was used as an index of microstructure deterioration. The samples were processed into cylinders and used after preheat treatment at 1500 °C in a coke breeze. The surface of the brick is covered with slag scattered by strong agitation during BOF operation. Therefore, the test was conducted under conditions in which the diffusion of the generated gas out of the system was moderate, as the reaction rate was considered to be excessive under the experimental conditions

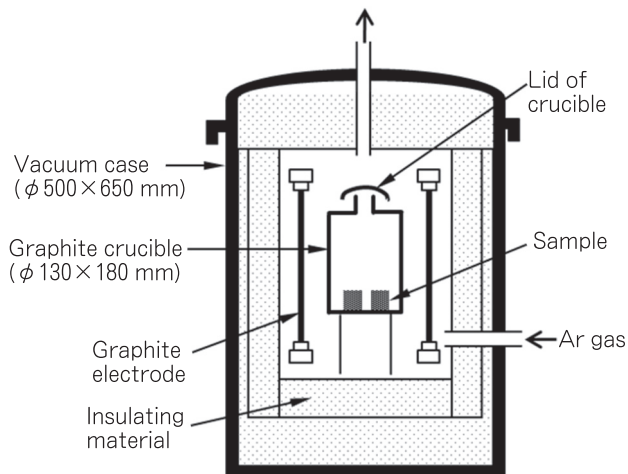


Fig. 4 Experimental apparatus of MgO-C reaction tests.

・気孔径分布

コークスブリーズ中で1500℃の熱処理したMgO-Cレンがを加工し、水銀圧入法により気孔径分布の測定を行った。

・MgO-C反応試験

MgO-C反応試験は、Fig.4に示す雰囲気焼成炉を用いて実施し、MgO-C反応試験で得られた重量減少率を組織脆化の指標として使用した。試料は、円柱状に加工したものをコークスブリーズ中で1500℃の事前熱処理し使用した。転炉操業中のレンが表面は、強攪拌によって飛散したスラグにより覆われている。従って、直接気流中に曝された実験条件では反応速度が過剰であると考え、より発生ガスの系外への拡散が緩やかな条件で試験を実施した。蓋をした黒鉛ルツボに試料を入れ、昇温速度 $10^{\circ}\text{C} \cdot \text{min}^{-1}$ で1650℃まで加熱した後、120 min保持し、室温まで空冷を行った。試験中は流量 $1 \ell \cdot \text{min}^{-1}$ のArガスで炉内を充填したが、試料はルツボ中のため直接Arガス気流に触れず、反応により発生したガスはルツボの蓋部分から少しずつ漏れる条件とし、加熱後の重量減少率をMgO-C反応に伴う変化として評価した。

・微構造観察

乾燥後の試料およびMgO-C反応試験後の試料の切断面の顕微鏡観察を行った。MgO-C反応試

in which the reaction was directly exposed to the Ar gas. A sample was placed in a graphite crucible on which light weight lid was putted, heated to 1650℃ at a temperature rising rate of 10°C and min^{-1} , held for 120 minutes, and air cooled to room temperature. During the test, the interior of the reactor was replaced with Ar gas at a flow rate of 1 liter and min^{-1} . Since the sample was in the crucible, it was not in direct contact with the Ar gas stream, the gas generated by the reaction was gradually leaked from the tiny gap between lid and the crucible, and the weight reduction rate after being heated was evaluated as a change due to the MgO-C reaction.

・Microstructure Observation

The microstructure of the dried sample and the cut section of the sample after the MgO-C test was observed.

3. Result

3. 1 General properties

The results of the general quality evaluations are shown in Fig. 5 - 9. The horizontal axis of each graph represents a value obtained by changing the particle size composition and indexing the surface area. The vertical axis represents the modulus of elasticity, modulus of rupture, a crushing strength, an apparent porosity and a bulk density. A linear approximation line was drawn in each graph to calculate a correlation coefficient. From the measurement results of the surface area, the modulus of elasticity, modulus of rupture, and compressive strength of MgO of 1.0 mm or less the measurement results of the sample after firing at 1600℃ showed a high correlation coefficient and showed a tendency to increase as the MgO surface area increased. When the apparent porosity and bulk density

験後の試料は樹脂に埋め込んだ後に加工し、微構造を観察した。

3. 結果

3. 1 一般品質

一般品質試験の測定結果をFig.5-9に示す。各グラフの横軸には粒度構成を変化させ表面積を指数化した値を、縦軸には弾性率、曲げ強度、圧縮強度、見掛け気孔率およびかさ比重を示す。それぞれのグラフにおいて線形の近似線を引き、相関係数を算出した。1.0mm以下のMgOの表面積と動弾性率、曲げ強度、圧縮強度の測定結果より、1600℃焼成後の試料の測定結果は相関係数が高く、MgO表面積が増えるに従い、やや高くなる傾向を示した。見掛け気孔率、かさ比重を比較すると乾燥後の試料では、MgO表面積との相関が高く、見掛け気孔率は高く、かさ比重は低くなる傾向を示した。1600℃焼成後の試料の見掛け気孔率はやや増加する傾向にあり、かさ比重はMgO表面積によらずほぼ一定の値を示した。

3. 2 通気率、気孔径分布

組織脆化は試料表面から進行し、脆化の要因となる各種の反応によって発生したガスの拡散のしやすさが組織脆化に影響すると報告されている^{2,5)}。通気率の測定結果をFig.10に、気孔径分布の測定に基づきそれぞれ3つの気孔径範囲(6 μ m以上、0.3 μ m以上6 μ m未満、0.3 μ m未満)に区分した気孔容積比率をFig.11に示す。通気率は概ね1.0mm以下のMgOの表面積の増加に従い低下していた。城塚ら⁶⁾もMgO-Cれんがの通気率は粒子径と圧損の関係よりKozeny-Carmanの式を用いて概ね説明できるとしており本結果においても同様の結果を示した。また、粒子径と圧損の関係と気孔容積比率は、MgO表面積の増加に伴い、試料全体の気孔容積がやや増加する傾向にあり、容積比率が異なることが明らかとなった。MgO表面積によらず、0.3 μ m以上6 μ m未満の気孔の容積は大きく変化しない一方で、6 μ m以上の比較的大きな気孔は容積が減少し、0.3 μ m未満の小さな気孔の容積が増加していた。従って、粒度の細かい

were compared, the samples after drying showed a high correlation with the MgO surface area, the apparent porosity was high, and the bulk density tended to be low. The apparent porosity of the samples after firing at 1600 °C tended to increase and the bulk density showed an almost constant value regardless of the MgO surface area.

3. 2 Permeability, pore size distribution

Microstructure deterioration progresses from the sample surfaces, and it has been reported that the ease of diffusing gases generated by various reactions that cause deterioration affects microstructure deterioration^{2,5)}. The measurement result of the permeability is shown in Fig. 10. Based on the measurement of the pore size distribution, the pore volume ratio, which is divided into three different pore sizes of 6 μ m or more, 0.3–6 μ m, and 0.3 μ m or less, is shown in Fig. 11. The permeability decreased with an increase in the surface area of MgO of approximately 1.0 mm or less. Jozuka et al. also explained that the permeability of MgO-C bricks can be roughly explained by using the Kozeny-Carman equation based on the relationship between the particle size and the pressure loss⁶⁾. In addition, the relationship between the particle diameter, pressure loss and pore volume ratio showed that the pore volume of the whole sample tended to increase slightly with the increase of the MgO surface area, and the volume ratio was different. Regardless of the MgO surface area, the volume of the pores of 0.3–6 μ m didn't change, while the volume of the relatively large pores of 6 μ m or more decreased, and the volume of the small pores of 0.3 μ m or less increased. Therefore, it was revealed that by increasing the proportion of fine particle size MgO the overall permeability

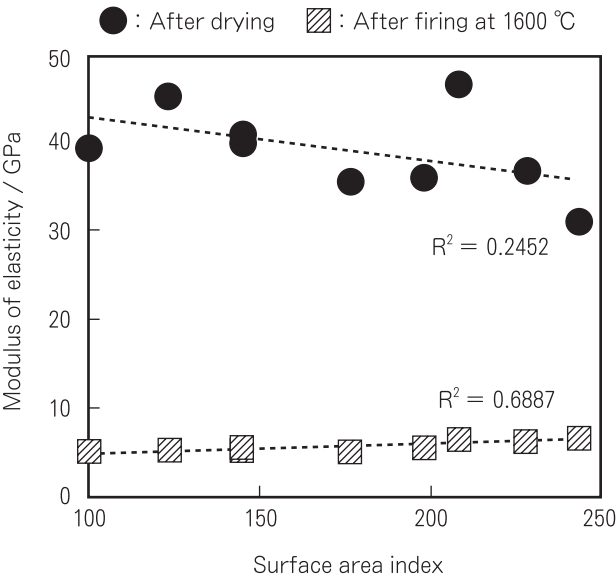


Fig. 5 Relationship between MgO surface area and modulus of elasticity of each sample.

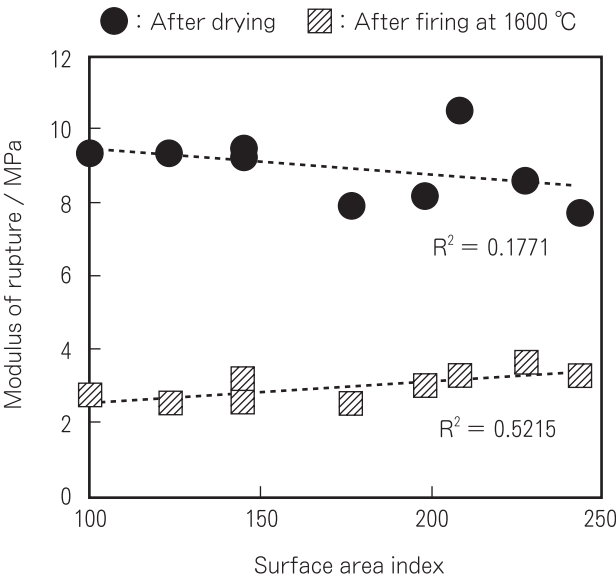


Fig. 6 Relationship between MgO surface area and modulus of rupture of each sample.

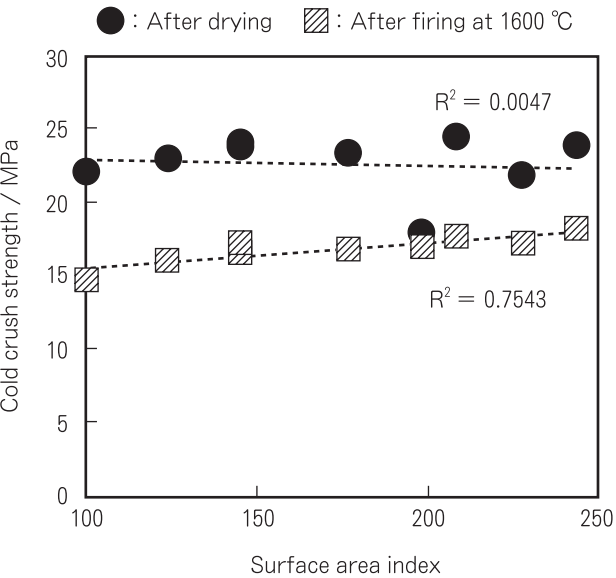


Fig. 7 Relationship between MgO surface area and cold crush strength of each sample.

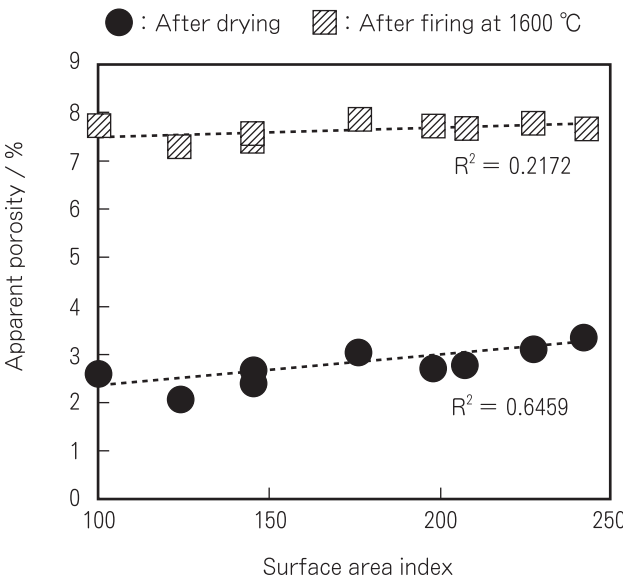


Fig. 8 Relationship between MgO surface area and apparent porosity of each sample.

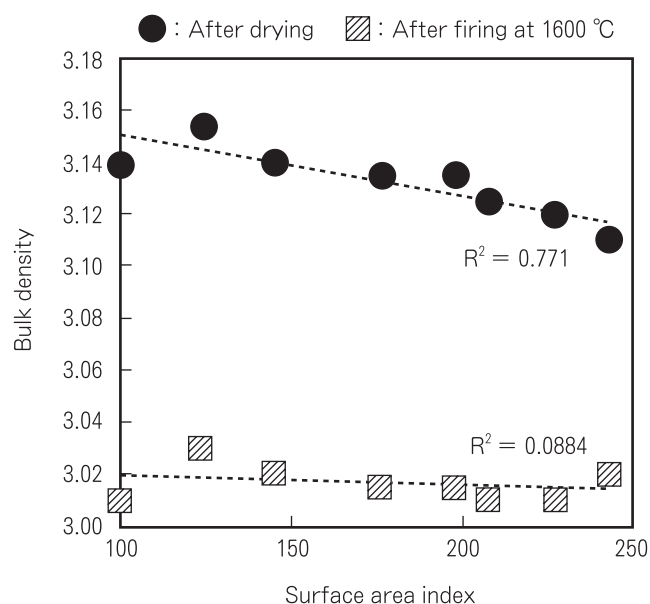


Fig. 9 Relationship between MgO surface area and bulk density of each sample.

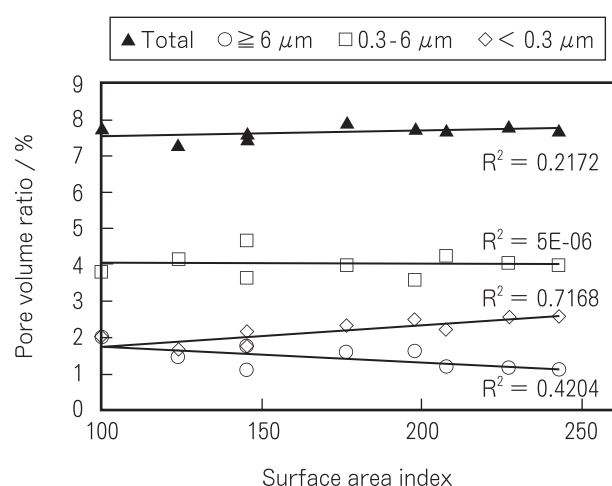


Fig. 11 Relationship between pore volume ratio and surface area index.

MgOの比率が増えることで、れんが全体の通気率が低下し、かつ大気孔の容積減少とともに、小気孔の容積が増加していることが明らかとなった。

3. 3 MgO-C反応試験

MgO-C反応試験後の重量減少率をFig.12に示す。この結果、微細なMgO比率の増加に伴い、重量減少率は増加する傾向を示した。しかしながら、No.1, 8 及び 9 などはこの傾向に当てはまら

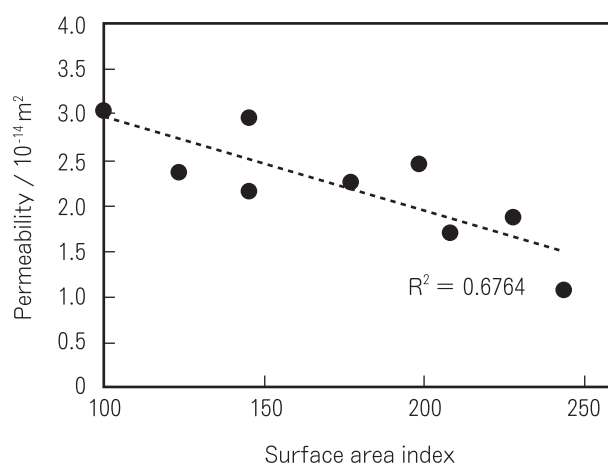


Fig. 10 Relationship between the permeability and surface area index.

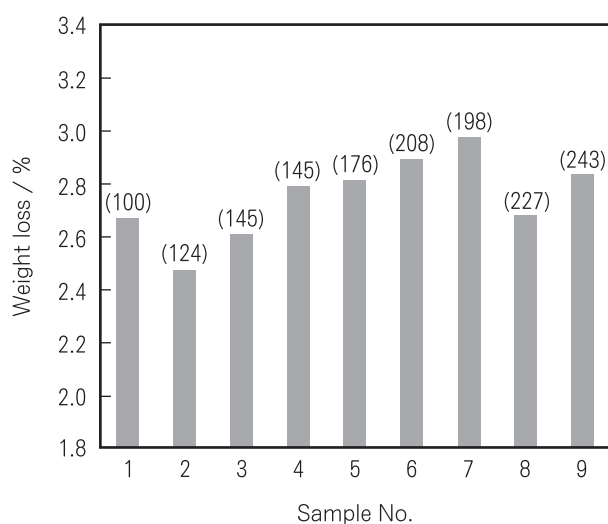


Fig. 12 Weight loss after MgO-C reaction test.

of bricks decreased, and the volume of the small pores increased as the volume of the large pores decreased.

3. 3 MgO-C reaction test

The weight reduction rate after the MgO-C reaction test is shown in Fig.12. The weight reduction rate tended to increase with the increase of the fine MgO ratio. However, No. 1, 8 and 9 don't apply to this tendency. No.2 exhibited the lowest weight reduction rate after

ない。また、試験後の重量減少率が最も低い値を示したのはNo.2の試料であり、この試料は粒度が最も細かい粒度cのMgOを含まず、表面積は標準試料のNo.1について小さい。

the test. This is the sample that didn't contain MgO, had the finest particle size c, and the surface area was the second smallest next to No. 1 of the standard sample.

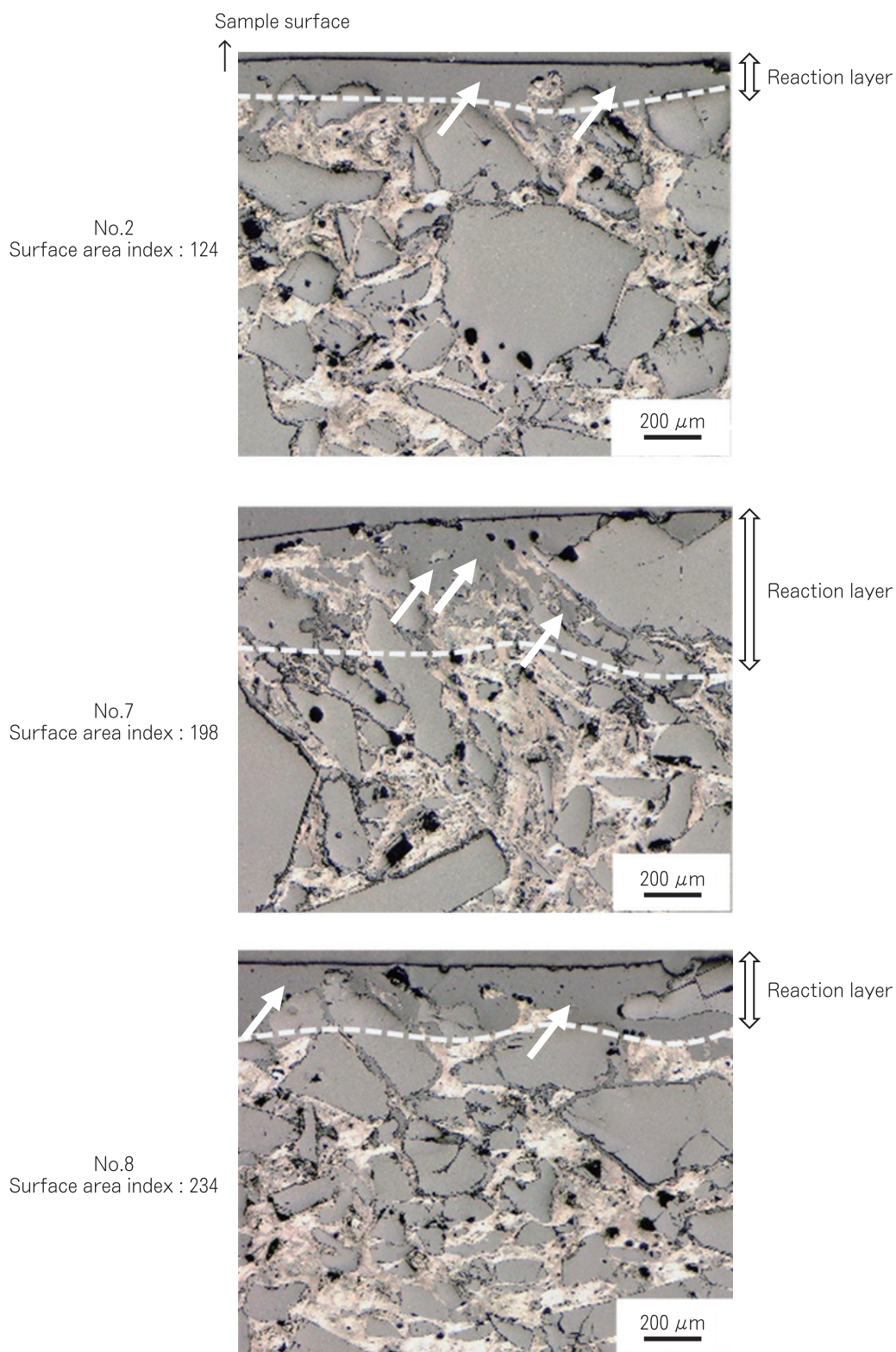


Fig. 13 Microstructure of each sample after MgO-C reaction test.

3. 4 微構造観察

MgO-C反応試験後の代表的な試料の反射顕微鏡写真をFig.13に示す。写真上部が試料表面に該当する。試料表面では、電融MgOと鱗状黒鉛の粒子境界に図中では矢印で示されるような空隙が形成されており、試料表面から内部にかけて脱炭層が形成されていた。MgO表面積が小さくMgO-C反応試験後の重量減少率の小さいNo.2とMgO表面積が大きく重量減少率の大きいNo.7の組織を比較するとNo.7の方がより脱炭層が厚い。一方で、No.7と更にMgO表面積の大きいNo.8とを比較するとNo.8の方が脱炭層の厚みが薄く、重量減少率の結果と一致していた。

4. 考察

MgO-C反応試験後の重量減少率や試験後の試料表面を観察すると、MgOの表面積が増加するに従い、重量減少率が大きくなり、反応に伴う組織脆化が認められた。しかしながら、表面積が大きい試料でも試験前後での重量減少率は小さく、また、反応に伴う組織脆化が少ない試料がある。そのため、単純なMgO表面積だけでは、れんがの組織脆化に及ぼす影響について整理が出来ず、他の因子も大きく関係している。

そこで、改めて、MgO表面積と通気率、気孔径の関係を整理した。Fig.14に、MgO表面積とMgO-C反応試験後の重量減少率を、また、図中の括弧内にてその試料の通気率を併せて示す。MgO表面積と重量減少率の関係をみると、通気率が同程度の試料であれば表面積の大きい試料の方が重量減少率は増加しており、MgO-C反応は表面積に影響していることが示唆された。一方、MgO表面積は大きいですが、組織脆化の小さい試料は通気率自体が小さくなっている。これは、れんが組織脆化に対しては通気率も大きく関与しており、れんが系外へガスが拡散する際の抵抗性が大きく影響しているものと考えられる。また、Fig.15に通気率と3つの気孔径範囲に区分した気孔容積比率の関係を示す。れんが中に存在する気孔径の大きさ別で比較すると、6 μm 以上の比較的大きな気孔に相関が認

3. 4 Microstructure observation

The microstructure photograph of a typical sample after the MgO-C reaction test is shown in Fig. 13. The upper side of the photograph corresponds to the surface of the sample. On the surface of the sample, voids as indicated by arrows in the figure were formed at the grain boundaries between the fused MgO and the graphite, and a decarburization layer was formed from the surface of the sample to the inside. Comparing the structure of No. 2, which had a small MgO surface area and a small weight reduction rate after the MgO-C reaction test, and No. 7, which had a large MgO surface area and a large weight reduction rate, the decarburization layer is thicker in No. 7. On the other hand, in No. 7 and No. 8, with large MgO surface area, the thickness of the decarburization layer was thinner in No. 8, which was consistent with the result of the weight reduction rate.

4. Discussion

When the weight reduction rate after the MgO-C reaction test and the surface of the sample after the test were observed, the weight reduction rate increased as the surface area of MgO increased, and microstructure deterioration accompanying the reaction was observed. However, samples with a large surface area had a small weight reduction rate before and after the test, and showed little microstructure deterioration due to the reaction. Therefore, the effects of bricks on microstructure deterioration can't be sorted out with MgO surface area alone. Not only MgO surface area but also other factors are also considered to be related to microstructure deterioration. The relationship of the MgO surface area, the permeability, and

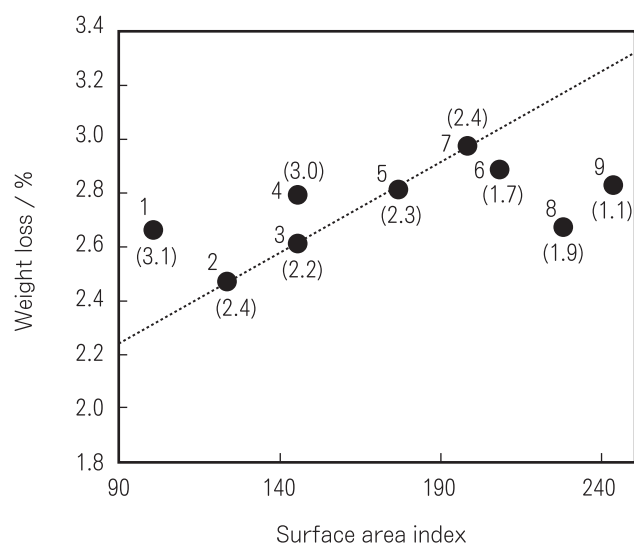


Fig. 14 Relationship between MgO-C reaction weight loss and surface area index with permeability.

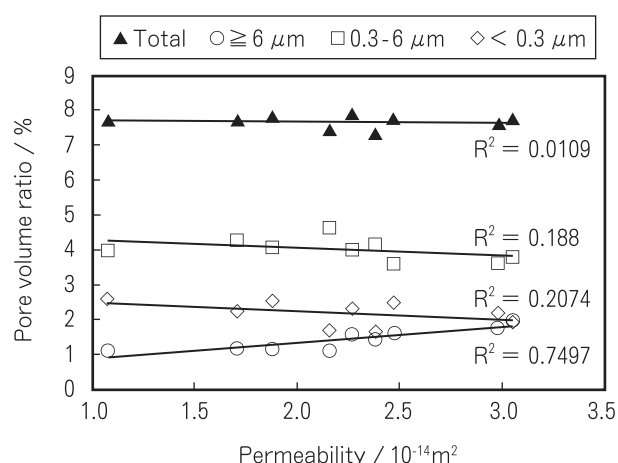


Fig. 15 Relationship between permeability and pore volume ratio.

められ、粒度構成が及ぼす通気率の変化には、これら大気孔の増加が最も影響しているものと考えられる。そのため、MgO-Cレンガの組織脆化対策としては、MgO表面積が小さく、かつ通気率を抑制可能な粒度構成などの採用が有効と考えられる。

the pore diameter was rearranged again. The MgO surface area, and weight reduction rate after the MgO-C reaction test are shown in Fig. 14. And parentheses in the figure is shown permeability of sample. Looking at the relationship between the MgO surface area and the weight reduction rate, the weight reduction rate increased in the samples having a larger surface area as long as the permeability was about the same. It was indicated that the MgO-C reactions had a direct effect on the surface area. On the other hand, the sample with little microstructure deterioration had a large MgO surface area but a little permeability. This is considered to be largely related to the permeability of the brick and microstructure deterioration, and to the resistance to diffusion of gas out of the brick to the outside of the system. The relationship between the permeability and pore volume ratio have been divided into three pore diameter ranges is shown in Fig. 15. Comparisons by size of pore size in the bricks revealed a correlation of relatively large pores of $6 \mu\text{m}$ or more. The increase of these large pores is considered to be most affected by the change in permeability caused by the particle size structure. In other words, it is considered that the use of a grain size distribution capable of reducing the MgO surface area and suppressing the permeability is considered to be effective as a microstructure deterioration countermeasure for MgO-C bricks.

5. Use Results in the Actual BOF

Based on the results of the above investigation, MgO-C bricks with increased porosity diameters in areas where MgO-C reactions are suppressed and air permeability is impeded were tested in a BOF at steel mill A. An index

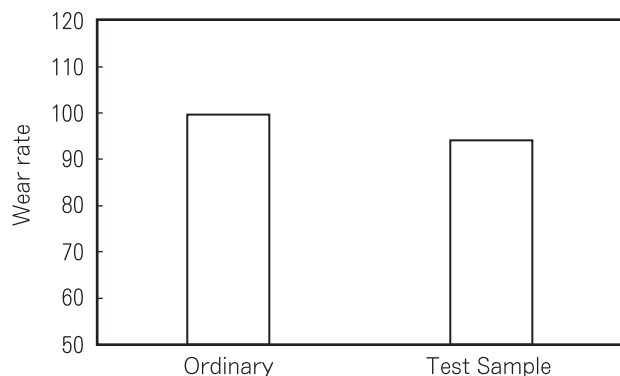


Fig. 16 Comparison of wear rate index of MHPs used in steel mill A.

5. 実機適用結果

上記の検討結果を踏まえ、MgO-C反応を抑制し、通気性を阻害する領域の気孔径を増加させたMgO-CれんがをA製鉄所の転炉にてテストを行った。テスト結果を指数化したものをFig.16に示す。従来材質と比較し損傷速度が約6%改善されおり通気性の低減は実機での耐用性改善に有効であると考えられる。

6. まとめ

MgOの粒度構成が組織脆化に及ぼす影響を明らかにするために1.0mm以下のMgOを篩い分けし、粒度構成を変化させた試料を作製し、評価を行った。この結果、MgO-C反応試験後の重量減少率、試験後の試料表面の観察結果から、MgOの表面積が増加するに従い、重量減少率が大きくなり、反応に伴う組織脆化が認められた。一方で、表面積が大きい試料でも試験後の重量減少率が小さく、また、反応に伴う組織脆化が少ない試料も見られた。MgO表面積と通気率、気孔径の関係を整理したところ、通気率が同程度の試料であれば表面積の大きい試料の方が重量減少率は増加しており、表面積はMgO-C反応に影響していることが示唆された。また、MgO表面積が大きくても組織脆化の小さい試料は通気率自体が小さくなっていることがわかった。これは、れんがが組織脆化に対して通気率も大きく関与しており、れんが系外へ

of the test result is shown in Fig. 16. Numbers in the vertical axis indicate wear rate. The wear rate was improved by about 6 % compared to the ordinary. In other words, the reduction of permeability is considered to be effective for improving the durability of the actual converter.

6. Conclusion

In order to clarify the influence of the grain size distribution of MgO on microstructure deterioration, samples in which the grain size distribution was changed by screening MgO of 1.0 mm or less were prepared and evaluated. As a result, from the weight reduction rate after the MgO-C reaction test and the observed results of the sample surface after the test, it was understood that the weight reduction rate increased as the surface area of MgO increased, and microstructure deterioration accompanying the reaction was observed. On the other hand, even in the samples having a large surface area, the weight reduction rate after the test was small, and the microstructure deterioration due to the reaction was small in some samples. When the relation between the MgO surface area, the permeability, and pore diameter was sorted out, it was indicated that the weight reduction rate increased in the sample having a larger surface area if the permeability was about the same, and that the MgO-C reactions had a direct effect on the surface area. In addition, it was found that the permeability itself was small in the sample having small microstructure deterioration even if the MgO surface area was large. It was inferred that the permeability also greatly contributed to brick microstructure deterioration, and that the resistance when the gas diffused out of the brick greatly influenced

ガスが拡散する際の抵抗性が大きく影響しているものと推察された。また、通気率と3つの気孔径範囲に区分した気孔容積比率の関係から、 $6\mu\text{m}$ 以上の比較的大きな気孔の容積と通気率に相関が認められ、粒度構成が及ぼす通気率の変化には、これら $6\mu\text{m}$ 以上の大気孔の増加が最も影響しているものと考えられる。

brick microstructure deterioration. In addition, a cordo relation was found among the permeability and the pore volume ratios that were divided into three pore diameter ranges the increased volume of large pores of $6\mu\text{m}$ or more had influence on the change of the permeability caused by the particle size structure.

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