

SHINAGAWA TECHNICAL REPORT

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報文／REPORT

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要 旨

高周波誘導炉に内張したMgO-Cれんがを、溶鉄を媒体として超高温(1800℃)まで加熱し、損傷させた結果、黒鉛量が損傷速度に影響を与えることがわかった。この損傷は、加熱面近傍におけるマトリックス空隙層形成とマグネシア粒子の溶鉄への流出という2つのステップからなることが推定された。空隙層の形成にはMgO-C反応が関与しており、黒鉛量によって稼働面の組織が温度に依存して変化し、反応ガスの移動性に影響を与えることが示唆された。

Abstract

It was clarified that the damage rate of MgO-C brick is influenced by graphite content by an investigative experiment in which MgO-C bricks relined in test vessel were heated up along with iron or steel to the Ultrahigh temperature up to 1800 °C in a high frequency induction furnace. It is inferred that the damage progressed in two steps, vanishment of the brick matrix near the heated surface associated with formation of a void region in the first step and the capture of the remaining coarse magnesia particles in molten metal in the second step. It is indicated that MgO-C reaction plays a role in void region formation and deterioration degree of brick structure near the heated surface. This depends on graphite content as well as on heating temperature, and influences the transience of gas phase generated by MgO-C reaction.

1. 緒言

鋼の精錬プロセスでは、反応効率の向上、スラグ排出量の削減、スクラップの利用拡大などを目的に、複数の容器に機能を分担させて段階的に処理する方法が広く採用されている¹⁾。転炉はその中核となる精錬容器であり、そこでは溶銑脱磷と脱炭を2つの容器で分割して行う処理^{2,3)}や、スクラップや鉬石を溶融還元した後に脱炭を別の容器で行う処理⁴⁾が行われる。このような機能分担した容器では、取り扱う溶鉄の処理温度範囲が異なるため、内張りされるMgO-Cれんがには、温度による損傷状況に応じた適切な

1. Introduction

The steel refining process, in which overall refining is carried out step-by-step in different furnaces or vessels with specialized refining functions and/or purposes is broadly applied in order to improve the efficiency of refining reactions, reduce total slag volume and expand the use of steel scrap¹⁾. A core refining facility is a converter furnace, in which hot metal dephosphorization and decarburization is carried out dividedly in two different furnaces^{2,3)}, or hot metal fabricated by smelting reduction of steel

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材料設計が要求される。

本報告では、高周波誘導炉を使用して、内張りしたMgO-Cれんがとその内部に鉄源を充填し、所定の温度となるまで昇熱し、反応・損傷させる実験を行った。加熱温度として、軽負荷操業を想定した1450℃と、高負荷操業を想定した1700℃および1800℃の3つの水準を設定し、黒鉛量と黒鉛種が異なるMgO-Cれんがの損傷速度を実験的に求め、損傷過程の違いを推定した。これらの結果について以下に述べる。

2. 実験方法

2. 1 供試試料

本試験に使用した黒鉛量(25%, 13%)と黒鉛種(A, B)の異なるMgO-Cれんが3種を、C25, C25S, C13Sと表記する。各材質の主要成分の値、代表的な物性値として1450℃還元焼成後(コークスブリーズ中)の気孔率、かさ比重の値をTable 1に示す。使用した黒鉛Aおよび黒鉛Bの粒子SEM画像をFig.1に示す。黒鉛Aはアコーディオン状⁵⁾、黒鉛Bは葉片状⁶⁾であることがSEM画像で確認できる。また、黒鉛Aは、黒鉛Bよりも、比表面積は大きく、約8倍の比表面積を持つ。

Table 1 Chemical and physical properties of three types of MgO-C brick samples

Sample		C25	C25S	C13S
Chemical composition				
MgO	/ %	71	71	83
C	/ %	25	25	13
(Graphite A)		○		
(Graphite B)			○	○
Physical properties after being fired at 1450 °C				
Apparent porosity / %		10.5	10.4	6.9
Bulk density		2.65	2.70	2.95

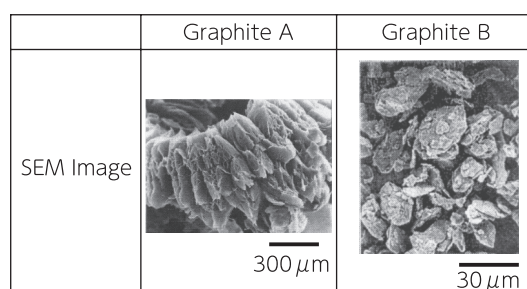


Fig. 1 SEM images of graphite A and graphite B.

scrap and/or iron ore in one furnace is sequentially decarburized in another furnace⁴⁾. Since the operation temperature among converter furnaces with such specialized functions differs greatly appropriate material design is necessitated for MgO-C bricks relined in the converter furnace with consideration on dominant damages in the corresponding operational temperature range.

MgO-C bricks were relined in a test vessel and an iron/steel source was filled in the test vessel. They were heated up to a specified temperature in order to investigate MgO-C brick damage as well as the reactions between brick and molten metal using high frequency induction furnace. Assuming low and ultrahigh operational temperatures in a converter furnace, three (3) levels of heating temperature, namely, 1450 °C, 1700 °C and 1800 °C, were selected as the utmost heating temperatures. The differences in the damage process were evaluated by investigating the damage rates of MgO-C bricks with different C content and/or different types of graphite. The details are described in this report.

2. Experiment

2. 1 Sample preparation

The major chemical and physical properties of three types of MgO-C brick samples with different C contents (25 % and 13 %) and different types of graphite (graphite A and graphite B) are summarized in Table 1. The MgO-C brick samples are labeled C25, C25S and C13S. The apparent porosity and bulk density of the MgO-C brick samples fired at 1450 °C in a coke breeze are shown in Table 1. As per Fig. 1, in which SEM images of graphite A and graphite B are shown, graphite A exhibits an accordion-shaped microscopic appearance⁵⁾ and the microscopic appearance of graphite B is foliate shape⁶⁾. It is noted that specific surface of graphite A is almost 8 times bigger than that of graphite B.

2. 2 Experiment equipment

As schematically illustrated in Fig. 2, MgO-C brick samples relined in a test vessel were heated up to a specified temperature in a high frequency induction furnace with roughly 8 kg of melting capability. More

2. 2 実験装置

本試験では溶融能力約8kgの高周波誘導炉を用いた。その模式図をFig.2に示す。炉内には上記の3材質C25, C25S, C13Sを各2枚, ダミー2枚の計8枚のれんがを所定の寸法に切断加工し, 内径 ϕ 128mm, 外径 ϕ 193mmとなるようライニングした。

2. 3 実験条件

試験温度を1450℃, 1700℃および1800℃の3水準とし, 溶解用の鉄源として, 1450℃では銑鉄(市販のデンスバー), 1700℃および1800℃はステンレス鋼(SUS430)を使用した。溶鉄の温度は, 連続測温用プローブを溶鉄中に浸漬してモニターしながら, 一定となるよう制御した。

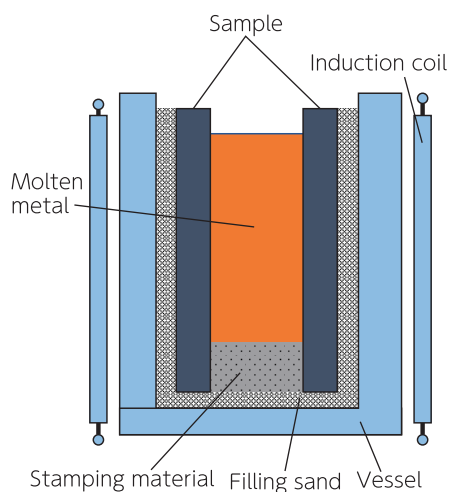


Fig. 2 Schematic diagram of heating test for MgO-C brick samples in high frequency furnace.

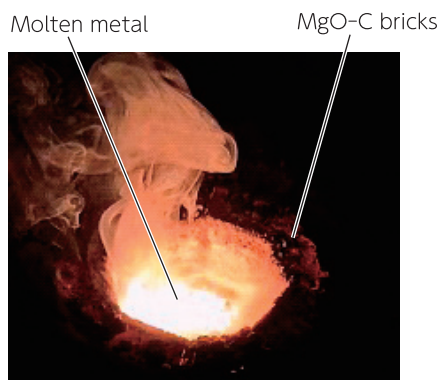


Fig. 3 Appearance of upper face of test vessel in high frequency furnace.

specifically, two pieces of each sample C25, C25S and C13S were relined in a test vessel along with two dummy bricks. Each relined brick sample was processed in advance so as to assemble cylindrical test vessel samples with ϕ 128 mm of inner diameter and ϕ 193mm of outer diameter.

2. 3 Experiment conditions

As previously described, temperatures of 1450 °C, 1700 °C and 1800 °C were applied for the heating test. As for the iron/steel source used in the test vessel, hot metal (commercially available dense bar) was used in the heating test at 1450 °C and stainless steel (SUS430) was used in the heating tests at 1700 °C and 1800 °C. The heating temperature was controlled by monitoring the temperature measured by a continuous temperature measuring probe which was dipped in the molten metal bath. Basically, the heating test was conducted for 5 hours. However, in cases where metal leakage by severe erosion of the relined bricks occurred the heating test was interrupted at that the time of occurrence. Since the major purpose of the heating test was to investigate the physical damage of MgO-C brick induced by molten metal as well as reactions inside the refractories, no erosive agent was added. The test vessel assembled with MgO-C brick samples was oscillated by eccentric rotation at 30 rpm rotation speed. Fig. 3 shows the appearance of the upper face of the test vessel in the heating test, during which fluctuation of the molten metal bath was observed.

2. 4 Evaluation method

Wear volume of the MgO-C brick samples undergoing the heating test was measured as per Fig. 4. H represents the metal line height, namely, the depth of the molten metal bath. The wear volume (V) was calculated with the measured wear area (S) and sample width (W). The damage rate or volume reduction rate (V_r) was calculated by dividing the wear volume by the heating test time. Afterwards, the cross sections of the MgO-C brick samples were observed along with microscopic observation of the damaged areas in the brick samples.

試験時間は最大5時間とし、試験中に内張りれんがの損傷量が大きく、漏鋼の危険があると判断された場合には、その時点で試験終了とした。なお、本試験では、MgO-Cれんがの高温状態での溶銑(または溶鋼)による物理的な損傷やれんが内部の反応に着目しているため侵食剤(スラグ)は使用せず試験を行った。試験中は30rpmで偏心回転をさせ、炉体を揺動した。Fig.3は試験中の状況を示し、一定の湯面変動を確認した。

2. 4 評価方法

試験後サンプルの損傷量測定方法をFig.4に示す。サンプルの損傷面積 S を測定し、サンプル幅 W として体積 V を求め、試験時間で割ることによって、損傷速度 V_1 を求めた。ここで、 H はメタルライン部の高さを示す。更に、切断後のサンプル外観、損傷部の微構造観察を行った。

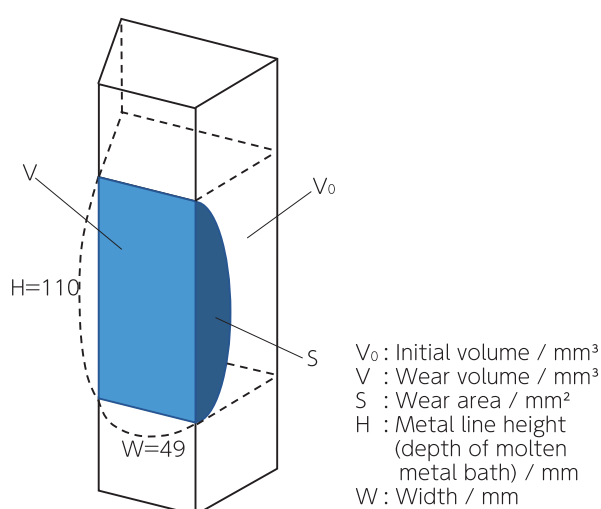


Fig. 4 Measurement of wear volume of MgO-C brick sample in heating test.

3. 結果

Fig.5にサンプルC25, C25S, C13Sの各試験温度での体積減少率を示し、Fig.6に1450℃, 1700℃, 1800℃試験後それぞれの切断面を示す。1450℃試験後のいずれのサンプルも僅かな損傷面であり、体積減少率も小さかった。一方、1700℃以上では黒鉛量により異なる傾向を示し、C25とC25Sの1800℃試験における体積減少率は1450℃試験後と比較して、13~15倍と大きくなった。1700℃および1800℃試験後のれんが切断面には湯面レベルを境として半円状の局部損傷がみられた。特に、C25とC25Sの試料では地金とマグネシア粒子が混ざりあった組織が局損

3. Results

The volume reduction rates of samples C25, C25S and C13S at each heating test temperature are comparatively shown in Fig. 5. The cross section of each MgO-C brick sample is compared and classified by heating test temperature in Fig. 6. The MgO-C brick samples that underwent the heating test at 1450 °C exhibited light damage with a small volume reduction rate. In association with C content, the MgO-C brick samples put through the heating test at over 1700 °C exhibited different damage patterns. The volume reduction rate of C25 and C25S samples in the heating test at 1800 °C grew markedly larger than those in the heating test at 1450 °C by a factor of 13-15. Semicircular localized damage was observed at the molten metal bath portion in the cross section of the MgO-C brick samples in the heating test at 1700 °C and at 1800 °C. Fragments mixed with metal and magnesia particles captured in localized damage areas were also observed in the cross sections of samples C25 and C25S.

The microscopic photographs of the damaged area in each MgO-C brick sample in the heating tests at 1450 °C and at 1800 °C are shown in Fig. 7 and Fig. 8, respectively. Except for a decarburized layer with <100 μm thickness on the hot face, no damage was observed in the microstructure of the MgO-C brick samples after the heating test at 1450 °C. While, a distinct difference in damage pattern was observed in the microscopic photographs of the damaged area in the MgO-C brick samples in the heating test at 1800 °C. The damaged area microstructure in sample C25 can be divided into three layers, that is, a unified region where washed-out magnesia particles are captured in metal (1st layer), a void region in which parts of the brick matrix have vanished (2nd layer) and the original brick refractory structure (3rd layer) from the hot face of brick sample. Three similar divided layers were observed in the damaged area microstructure in sample C25S. While, sample C13S exhibited only 2nd and 3rd layer in its microscopic photograph of the damaged area it retained a wider range of

部に噛みこんでいた。

1450℃および1800℃試験後サンプルC25, C25S, C13Sの局損部の顕微鏡写真をそれぞれ、Fig.7およびFig.8に示す。切断面と同様1450℃試験後の稼働面には100μm未満程の薄い脆化層がみられる程度で、損傷は極めて軽微だった。一方、1800℃試験後のC25またはC25SとC13Sの組織には明確に違いがみられた。サンプルC25の微構造をみると、3層に大別でき、稼働面から順に、溶鉄中にマグネシア粒子が流出して一体化した組織(第1層)、空隙層(第2層)、原れんが組織(第3層)であった。C25S

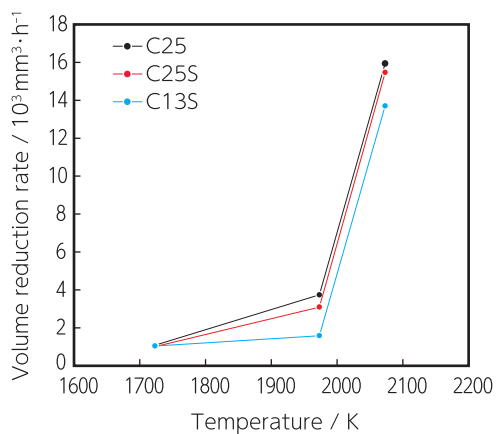


Fig. 5 Volume reduction rate of samples C25, C25S and C13S at each heating test temperature.

healthy brick structure than sample C25 or C25S. In short, the degree of damage induced by molten metal in samples C25 and C25C characterized by high graphite content was much more severe than that in sample C13S. When comparing sample C25 blended with graphite A with sample C25S blended with graphite B, sample C25 exhibits slightly more severe deterioration in the original refractory brick structure than sample C25S with almost equivalent thickness of void region (2nd layer).

4. Discussions

Based on the experiment results, it is inferred that MgO-C brick damage by molten metal at ultrahigh temperatures progresses, in two steps as schematically illustrated in Fig. 9. That is, early on, the brick matrix composed of fine magnesia and graphite particles disappears and a void region is formed as shown in the first step framed with a blue color line. This is followed by the capture of the remaining coarse magnesia particles into the molten metal in the second step, framed with red color line. Unlike fired refractory brick with a structure tightly upheld by a ceramic bond, MgO-C brick structure is sustained by carbon bond derived from the resin used as binder and mechanical

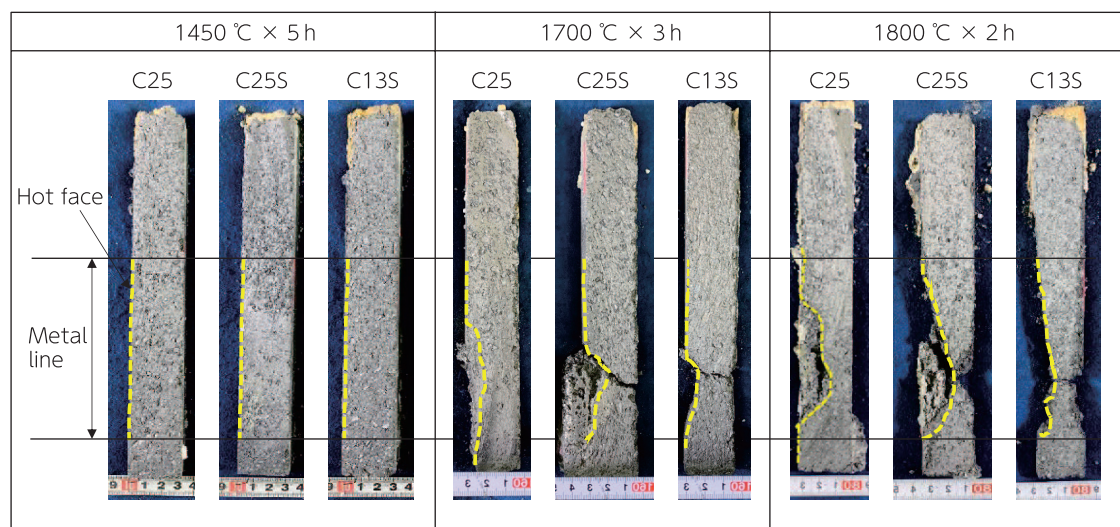


Fig. 6 Cross section of each MgO-C brick sample experiencing heating test at 1450 °C, 1700 °C and 1800 °C.

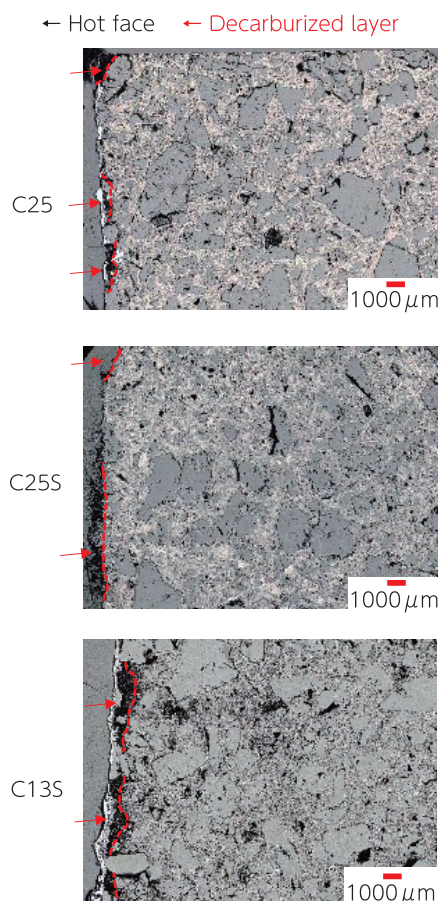


Fig. 7 Microscopic photographs of damaged area in each MgO-C brick sample in heating test at 1450 °C.

の微構造では、C25と同様、これらの層が確認できた。一方、C13Sの微構造には、第2層、第3層のみがみられ、C25やC25Sと比較すると、健全な組織を維持していたと考えられる。総括すると、黒鉛量の多いC25およびC25Sの組織脆化の程度がC13に比較して大きく、更に黒鉛種AおよびBを使用したC25はC25Sでは、C25の原れんが層の脆化の程度がC25Sと比較してやや大きいものの、C25の空隙層厚みはとC25Sと比較してその差は小さかった。

4. 考察

上記の結果から、超高温におけるMgO-Cれんがの損傷メカニズムについて以下のような2つのステップを考えた。その模式的にFig.9に示す。これらの2つのステップは、れんが組織中のマグネシアと黒鉛からなるいわゆるマトリックス部分の消失が進行して空隙層が形成されるステップ(STEP1：青枠囲み部)と、残留したマグネシア粗粒子がれんが組織から流出し、溶鉄に取り込まれるステップ

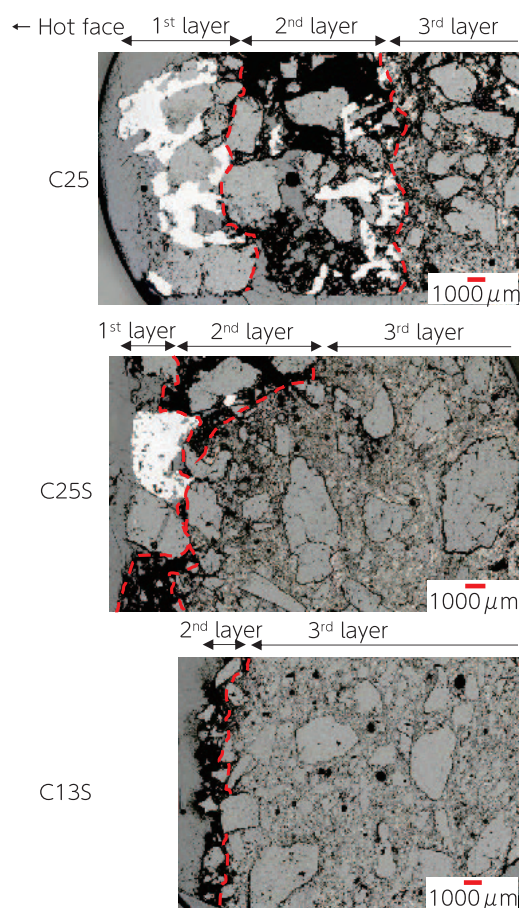
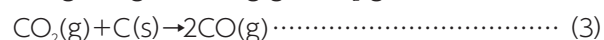
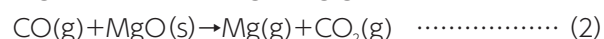


Fig. 8 Microscopic photographs of damaged area in each MgO-C brick sample in heating test at 1800 °C.

compaction. Therefore, it is expected that after first step progresses to a certain extent, the force to maintain the brick structure will be less than the stirring force of the molten iron, and second step will easily progress.

Among the variety of proposed mechanisms for the formation of a void region in MgO-C brick at ultrahigh temperatures under reduction atmosphere^{7,8)}, the MgO-C reaction, oxidation-reduction reaction between MgO and C, is acknowledged as an established theory. The MgO-C reaction is expressed with equation (1), which comprises equation (2) and (3).



It can be comprehended that the MgO-C

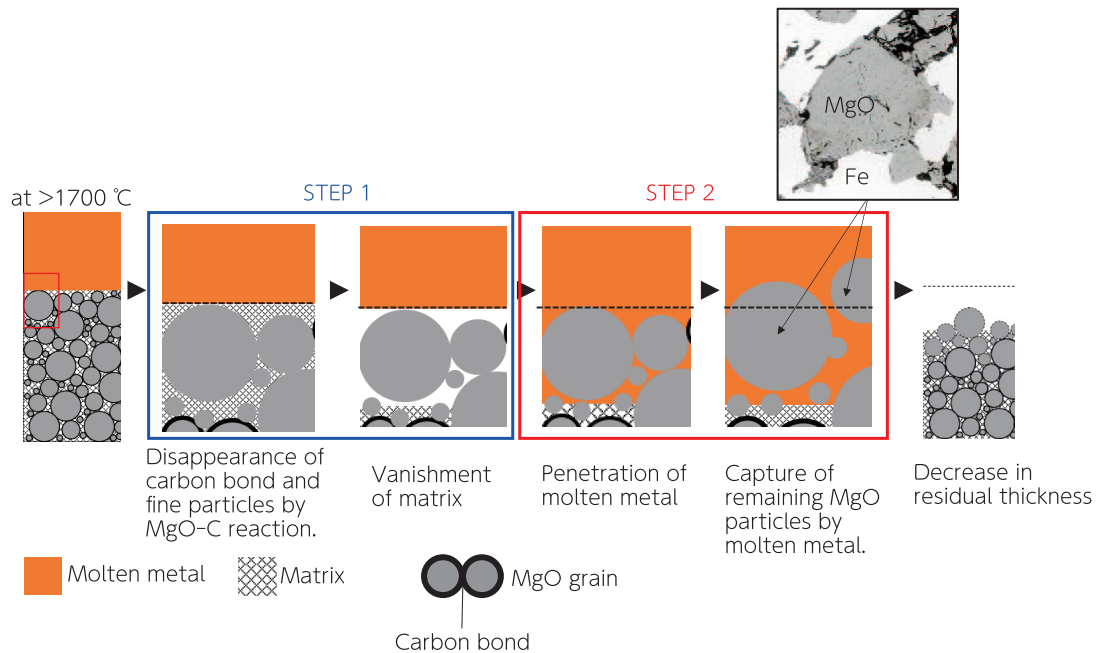
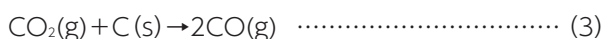
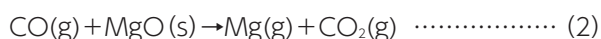
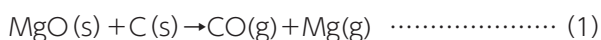


Fig. 9 Schematic illustration of wear mechanism of MgO-C brick at ultrahigh temperature.

(STEP2：赤枠囲み部)である。MgO-Cれんがは、焼成れんがのようなセラミックス結合とは異なり、バインダーとして使用される樹脂由来のカーボン結合と圧密によって組織が維持される。そのため、ステップ1がある程度進行すると、れんが組織の維持力が溶鉄の攪拌力より下回り、ステップ2が容易に進行していくことが予想される。

超高温・還元雰囲気下でMgO-Cれんが中に空隙層が形成される現象について、様々な報告があり^{7,8)}、中でも、MgO-C反応と呼ばれるマグネシアとカーボンの酸化還元反応がその定説として扱われることが多い。このMgO-C反応は、次の式(1)で表され、更にこの式(1)は、式(2)および(3)から構成されている。



ここで、式(1)で表される反応は、固体(MgO-C)からCO, Mgガスへの熱分解反応とみなすことができる。固体の熱分解反応速度を求めるため、溶液反応における濃度変化の代わりに分解率 α を導入し、時間 t における分解率 α は、次式(4)のように示すことができる^{9,10)}。

reaction expressed with equation (1) is a thermal decomposition reaction from solid phase (MgO and C) to gas phase (CO and Mg gas). To calculate thermal decomposition rate of solid phase, decomposition reaction rate (hereinafter referred to simply as “reaction rate”), α , which is coordinative term of concentration change rate in liquid phase reaction, was introduced. Reaction rate, α , at time, t , is expressed as per equation (4)^{9,10)}.

$$\frac{d\alpha}{dt} = k \cdot f(\alpha) \quad \text{..... (4)}$$

With integrating equation (4), equation (5) is obtained.

$$F(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} = kt \quad \text{..... (5)}$$

Where, k and $f(\alpha)$ respectively represents reaction rate constant and function depending on rate-determining step of the reaction. Based on this reaction model, a variety of functions, $f(\alpha)$, are suggested^{9,10)}. Presuming that the reaction process in which generated gas phase diffuses through solid phase and finally effuses out of the system is regulated by one-dimensional diffusion, α^2 is

$$\frac{d\alpha}{dt} = k \cdot f(\alpha) \quad \dots\dots\dots (4)$$

更に、これを積分すると次式(5)のように表すことができる。

$$F(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} = kt \quad \dots\dots\dots (5)$$

ここで、kは速度定数、f(α)は律速段階に依存する関数である。f(α)は種々の反応モデルに基づいて様々な関数が導かれており^{9,10)}、気体生成物が固体生成物中を拡散して系外に放出される過程を1次元的拡散律速であるとみなして、F(α)としてα²を選定した。すなわち、式(5)は、式(6)のように表すことができる。

$$\alpha^2 = kt \quad \dots\dots\dots (6)$$

そこで、実験で得られた損傷速度V₁から、体積減量率V₁/V₀を求め、これを反応率αとした。式(6)から、サンプル毎に各試験温度における反応速度定数kを算出した。その結果をTable 2に示す。さらに、得られた速度定数から、広く知られるアレニウスの式を用いて反応の温度依存性を評価した。アレニウス式を自然対数の形に表すと、

$$\ln(k) = \ln(A) - \frac{E}{RT} \quad \dots\dots\dots (7)$$

selected as f(α). Consequently, equation (5) was rewritten as per equation (6).

$$\alpha^2 = kt \quad \dots\dots\dots (6)$$

In this study, using volume reduction rate, V₁, which was obtained from heating test, volume reduction rate, V₁/V₀, was deemed as the reaction rate, α. Thus, reaction rate constant, k, of MgO-C brick samples at each heating test temperature were calculated. The calculation results are summarized in Table 2. The temperature dependency of reaction was evaluated by inserting calculated reaction rate constant, k, into well acknowledged Arrhenius equation. Arrhenius equation in natural logarithm form is expressed as per equation (7),

$$\ln(k) = \ln(A) - \frac{E}{RT} \quad \dots\dots\dots (7)$$

where,

k : Reaction rate constant

A : Frequency factor

E : Activation energy

R : Gas constant

T : Temperature

As per Fig. 10, the calculation results of three types of MgO-C brick samples are plotted on an Arrhenius plot with “1/T” horizontal axis and “ln(k)”

Table 2 Results of experiment data calculation for Arrhenius plot

Sample	T		10 ⁴ /T	V ₁	α	k	ln(k)
	℃	K	K ⁻¹	mm ³ ·h ⁻¹	%	sec ⁻¹	
C25	1450	1723	5.804	1078	0.527	0.278	-1.282
	1700	1973	5.068	3737	1.827	3.336	1.205
	1800	2073	4.824	15939	7.790	60.691	4.106
C25S	1450	1723	5.804	1006	0.492	0.242	-1.420
	1700	1973	5.068	3090	1.510	2.282	0.825
	1800	2073	4.824	15470	7.561	57.172	4.046
C13S	1450	1723	5.804	1042	0.509	0.259	-1.349
	1700	1973	5.068	1581	0.773	0.597	-0.515
	1800	2073	4.824	13704	6.698	44.861	3.804

T : Temperature V₁ : Volume reduction rate α : Reaction rate k : Reaction rate constant

となり、ここで、

k：反応速度定数

A：頻度因子

E：活性化エネルギー

R：気体定数

T：温度

である。

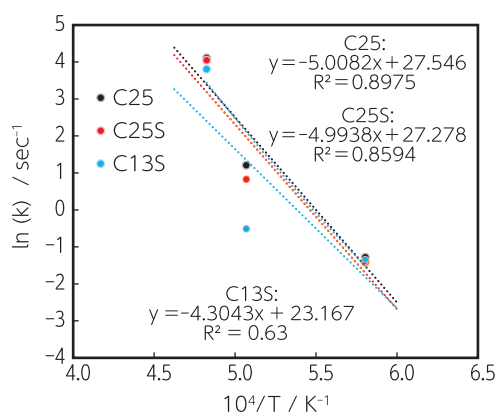


Fig. 10 Arrhenius plot of each MgO-C brick sample calculation data.

Table 3 Activation energy (E), term of frequency factor (ln(A)) and correlation coefficient (r) of each MgO-C sample obtained by Arrhenius plot

	$-E/R \times 10^4$	E (kJ/mol)	$\ln(A)(\text{sec}^{-1})$	-r
C25	5.0082	416.4	17.5	0.9474
C25S	4.9938	415.2	17.2	0.9270
C13S	4.3043	357.9	13.1	0.7937

先の計算結果を基に、Fig.10に $1/T$ を横軸、 $\ln(k)$ を縦軸としたアレニウスプロットを示す。このプロットから、活性化エネルギーE、頻度因子 $\ln(A)$ 、相関係数rが得られた。その結果をTable 3に示す。サンプルC25およびC25Sの各値はおおむね一致し、かなり良い直線性を持つ回帰直線が得られた。一方、サンプルC13Sの各値はC25およびC25Sとは異なる値を示した。また、その相関係数はこれらと比較するとやや低かった。アレニウスプロットの回帰直線の直線性は、決定した関数に対する一致性を示すことから、C13Sのプロットが比較的直線にならなかったことは、律速段階が異なり、反応速度が物質移動速度として観測されている可能性がある。

vertical axis. Classifying with MgO-C brick sample, activation energy (E), term of frequency factor ($\ln(A)$) and correlation coefficient (r) obtained with Arrhenius plot are summarized in Table 3. Calculated two major parameters, E and $\ln(A)$, for damaging reaction of MgO-C brick (or MgO-C reaction) in sample C25 and C25S conform to each other with a high correlation coefficient of regression curve. E and $\ln(A)$, which are the damaging reaction of MgO-C brick in sample C13S differ from those in sample C25 and C25S with lower correlation coefficient of regression curve. Since the correlation coefficient of regression curve indicates conformity to the reasonability of the presumption that α^2 is appropriate as function ($f(\alpha)$) to express the rate-determining step of the reaction. The fact that the sample C13S plot is relatively nonlinear indicates that the reaction rate may be observed as a mass transfer rate.

The progress of MgO-C reaction consists of thermal decomposition of solid into gas phase and effusion of generated Mg and CO gas out of system. For this reason, it is purported that the progress of MgO-C reaction is influenced by various properties of MgO-C brick, such as porosity, permeability, specific surface area of particles, and purity of blended raw materials^{11,12)}. In a model proposed by S. C. Carniglia et al.¹³⁾, for example, it is explained that diffusion of generated gas regulates the overall reaction. Furthermore, it is indicated in precedent investigation works by Doi et al.¹⁴⁾ that MgO-C reaction is influenced by porosity and permeability of MgO-C brick. Even when the test temperature is raised, the thickness of the void region observed on the hot surface in sample C13S is not varied so much as those of sample C25 and C25S. It is inferred that, since the void region thickness of sample C13S did not change much in the heating test at 1450 °C and 1700 °C, the effusion of gas was suppressed, resulting in less damage. When sample C25 blended with graphite A, and sample C25S blended with graphite B, are compared the deterioration degree of the original refractory brick structure in sample C25 was slightly more severe

MgO-C反応の進行は、反応自体の起こる過程と、反応後に生成したMgガスやCOガスが系外に放出される過程がある。そのため、れんが特性の内、気孔率や通気率、粒子表面積、原料純度等様々なパラメーターが関与するとされている^{11,12)}。例えば、S.C.Carnigliaら¹³⁾のモデルでは、反応後生成物のガス拡散が反応の律速であると説明されている。また、当方らの過去の実験的研究においても、気孔率や通気率の大小がMgO-C反応を抑制することが示唆される結果が得られている¹⁴⁾。サンプルC13Sの試験後稼働面表層にみられた空隙層厚みは、加熱温度が上昇しても、C25、C25Sと比較すると変化が少なかった。そのため、C13Sの1450℃および1700℃の試験温度では、空隙層厚みが変化せず、透過するガスの拡散を阻害したために、反応が進行しにくかったためと考えられる。一方、黒鉛種AおよびBを使用したC25とC25Sとの比較では、C25の原れんが層の脆化の程度がC25Sとやや大きいものの、透過するガスの拡散を阻害する程でなく、反応速度定数や活性化エネルギーなどに差がみられなかったのではないかと推察する。

5. まとめ

高周波誘導炉を使用して、超高温(1800℃)でのMgO-Cれんがの損傷を実験的に再現し、以下の知見を得た。

- ・加熱試験によるC25、C25Sの損傷速度は、温度上昇に伴って比較的直線的に増加したが、C13Sの損傷速度は、緩やかに増加した。
- ・サンプルC25およびC25Sの微構造には、稼働面から順に、溶鉄にマグネシア粒子が流出した組織(第1層)、空隙層(第2層)、れんが組織(第3層)がみられた。
- ・サンプルC13Sの微構造には、上記のうち、わずかな第2層と第3層がみられ、C25やC25Sと比較して、稼働面の空隙層厚みは小さかった。
- ・上記結果から、1800℃での超高温での損傷メカニズムについて以下のような2つのステップを考えた。
STEP1: MgO-C反応による、れんが中のマトリックスが消失する。
STEP2: マグネシア粒子がれんが組織から流出して、溶鉄に取り込まれる。
- ・得られた実験データを基に、MgO-C反応における反応速度の温度依存性をアレニウスプロットで評価したところ、サンプルC25、C25Sに対してC13Sと直線性に違いがみられ、超高温においても組織の健全性を維持してい

than that in sample C25S. It is inferred that, because of the small influence of original refractory brick structure deterioration degree on the diffusion of generated gas, no differences are observed in reaction rate constant (k) and activation energy (E) between sample C25 and C25S.

5. Conclusion

A heating test on MgO-C bricks at 1800 °C was conducted using high frequency induction furnace so as to reproduce damage by molten metal, and the following results/conclusions have been obtained.

In accordance with the elevation of heating test temperature, the damage rate (volume reduction rate) of sample C25 and C25S increased almost linearly. While, the damage rate of sample C13S gradually increased.

In the damaged area microstructure of samples C25 and C25S in the heating test at 1800 °C, a unified region where washed-out magnesia particles were captured in metal (1st layer), a void region, in which parts of brick matrix are vanished (2nd layer) and the original brick refractory structure (3rd layer) were observed from the hot face of brick sample.

In the damaged area microstructure of sample C13S in the heating test at 1800 °C, only the 2nd and 3rd layers were observed, and the void region thickness was smaller than those of samples C25 and C25S.

Based on the experiment results, it is inferred that the molten metal damage mechanism of MgO-C brick at ultrahigh temperatures proceeds by two steps, vanishment of brick matrix structure (Step 1) and capturing of remaining magnesia particles into molten metal (Step 2).

Evaluation of the temperature dependency of the reaction by Arrhenius plotting of the experiment data revealed the difference in the correlation coefficient of the regression curve between sample C25/C25S and sample C13S. The reaction rate of C13S, which maintained its microstructural integrity even at ultrahigh temperatures, could have been observed as a mass transfer rate.

The above results/conclusions are useful for

たC13Sの反応速度は、物質移動速度として観測されている可能性がある。

1800℃といった超高温操業が含まれる精錬炉のMgO-Cレンガを設計する場合、本実験結果を考慮し、最適な黒鉛量や物理特性を決定することができる。

resolving the problem of suitable graphite content or other adequate MgO-C brick physical properties in material design work for MgO-C brick to be used in refining furnaces with ultrahigh operational temperatures close to 1800 °C.

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