

SHINAGAWA TECHNICAL REPORT

環境に配慮したリサイクルMgO-Cれんが “Green Refractory” シリーズ

Environmentally Friendly Product
— MgO-C Green Refractories —

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製品紹介／PRODUCT

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要 旨

MgO-Cれんがのリサイクル用途の拡大を目的に、転炉で内張りされた高グレード使用済みれんがを原料として再資源化するプロセスを確立し、得られたリサイクル原料を一定量使用したMgO-Cれんがを開発した。当開発品は当社がGreen Refractoryと名付けて推進を図っている環境配慮型商品の1つであり、各種製鋼炉への適用、拡大により原料製造時のCO₂排出量削減効果が期待できる。

Abstract

By establishing a recycling process to convert used high-grade MgO-C bricks from BOF converter linings into recycled MgO-C raw materials, an environmentally friendly product “MgO-C Green Refractories”, which contains the recycled MgO-C raw materials in a specific blend ratio, has been developed. In the production process of electro-fused magnesia, which is one of the main raw materials of MgO-C bricks, a large amount of electric power is required for the electric arc melting process. Therefore, the use of the “MgO-C Green Refractories” in various steelmaking furnaces and vessels is connected to the reduction of CO₂ gas emissions. Through the promotions and expansions of “MgO-C Green Refractories”, we will contribute to the realization of a sustainable decarbonized society.

1. 緒言

製鋼工程において稼働する各種精錬設備には、その使用条件に対応した様々な耐火物が使用されている。近年では、カーボンニュートラルを実現する脱炭素化への取り組みが企業の経営目標に掲げられており、当社においても使用後耐火物や他産業で発生するパイプロダクトなど実質的にCO₂排出をゼロとみなすことができる原料を20mass%以上含有する耐火物を「グリーンリフラクトリー (Green Refractory)」と名付け製品の開発を推進している。その実行策の1つとして、転炉、RHなどの主要な精錬設備において内張り材として使用されるマグネシアカーボンれんが(以下、MgO-Cれんが)の使用後品を用いたGreen

1. Introduction

Various kinds of refractories are used in steel-making facilities in accordance with application purposes and operational conditions. Based on the corporate business objective to contribute to the establishment of a decarbonized society, achieving carbon neutrality, the author's company, Shinagawa Refractories Co. Ltd., has recently been engaged in the development of environmentally friendly refractory products into which over 20 % recycled raw materials, such as used refractories generated in refractory consuming industries as well as by-products or regenerated materials generated in various industries, which can be qualified with substantially zero CO₂ emission are blended. These

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Refractoryの開発に取り組んでいる。MgO-Cれんがは、その解体量も多いため、資源としての有効活用が期待される。

MgO-Cれんがのリサイクル用途として、製鉄副原料や不定形耐火物用リサイクル原料として還元、あるいは埋設処理することなどが行われている^{1, 2, 3)}。MgO-Cれんがへリサイクル原料を還元する報告例もいくつかあるが^{4, 5)}、リサイクル時に混入される不純物の耐火物品質低下への影響や、経済的合理性などを考慮するとその適用は限定的である。そこで当社では、転炉で内張りされた高グレード使用済みMgO-Cれんがを原料として再資源化するプロセスを確立することで、MgO-CれんがのGreen Refractoryを開発したので紹介する。

2. 再資源化プロセスとMgO-Cリサイクル原料

使用済みMgO-Cれんがから、リサイクル原料が出来るまでのフローをFig.1に示す。

- ① 解体された使用済みれんがを回収する。
- ② 回収されたれんがを所定の場所まで運搬し、保管する。
- ③ 永久張りれんが（マグネシア質れんが）と分別後、れんが稼働面付着物を除去し、残部を回収する。
- ④ 所定の粒度になるように粉砕、分級する。
- ⑤ 更に磁力選別、乾燥を行い、混入した不純物や含有水分を除去する。
- ⑥ 検査に合格したものをリサイクル原料とする。

environmentally friendly refractory products are called “Green Refractories”, and various types of “Green Refractories” have been developed. As part of such development work, MgO-C Green Refractories in which used MgO-C refractories applied as relining materials for major refining facilities, such as the converter furnace or RH type vacuum degassing vessel, are blended as recycled raw materials has been developed. Because of the large amount of demolished MgO-C refractories, effectiveness of their recycling application on conserving of natural resources is highly anticipated.

Used MgO-C bricks removed from furnaces or vessels have been recycled as sub-materials for refining operation, roadbeds or used as raw materials for monolithic refractory products^{1, 2, 3)}. Even though parts of used MgO-C refractories are recycled as raw materials for MgO-C bricks^{4, 5)}, negative influences of contamination by impure elements contained in used bricks on qualities of refractory products are concerned in view of overall economic rationality. The author's company developed MgO-C Green Refractories by establishing an efficient recycling process of used high-grade MgO-C bricks which are relined in converter furnaces. The details of development works are introduced in this article.

2. Used MgO-C Brick Recycling Process

Fig.1 shows recycling process of used MgO-C bricks. After being removed from furnaces or vessels, the retrieved pieces of used MgO-C

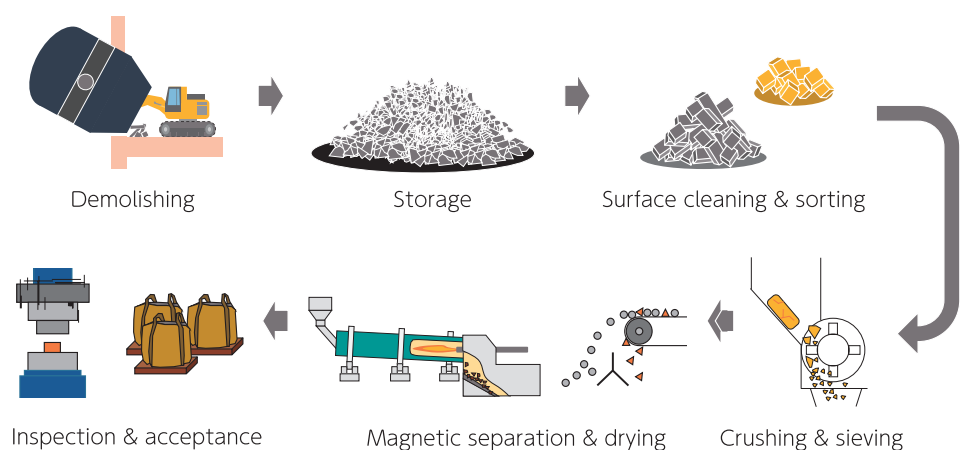


Fig. 1 Recycling process of used MgO-C bricks to raw materials.

上記フロー内において、回収元で予め大きな鉄片、スラグ、異種材等が分別され、更に回収後、熟練した作業者による手選別・ケレン作業（れんが稼働面に付着した異物を除去する作業）の徹底により、良質なリサイクル原料が得られる。

得られたリサイクル原料の外観写真をFig.2、顕微鏡写真をFig.3に示す。リサイクル原料は、未使用のMgO-Cれんがと同色の黒色を示し、粉碎粒度が細くなるほど白味が増し灰色となった。顕微鏡写真においては、2種類の形態の粒子が存在することが確認でき、1つは電融マグネシア粒、もう1つは黒鉛粒子と電融マグネシア粒子からなる複合粒子集合体であった。電融マグネシア粒は原料の状態とほぼ変わらず、高純度原料である大結晶粒もそのまま観察された。また、結晶粒の変質や外来成分の浸潤もみられなかった。次に、リサイクル原料の物理特性および化学組成

bricks are temporarily stored and subject to the separation of the demolished fragments of the used magnesite bricks which had been used for relining in a permanent layer. Then, the surfaces are cleaned by removing adhering materials. The surface-cleaned used MgO-C bricks are crushed and sieved so as to sort into specified particle sizes. After that, the crushed particles of the used MgO-C bricks are processed in magnet separation unit and dryer for removing immixed impurity elements and moisture components. After certified by acceptance inspection, particles of used MgO-C bricks with specified particle sizes are recycled as reborn raw materials of MgO-C Green Refractories.

Exterior appearances and microscopic photograph of recycled raw materials reborn from used MgO-C bricks are shown in Fig. 2 and Fig. 3, respectively. Similar to unused MgO-C brick, recycled raw material from used MgO-C bricks is blackish in color, which gradually recedes to grey color in association with reduction in particle size. The microscopic photographs of recycled raw materials exhibits two major kinds of particles, fused magnesite particles and MgO-C aggregate particles which are composed of fused magnesite and graphite. The appearance of fused magnesite particles in recycled raw materials is almost similar to that of original fused magnesite particles blended in MgO-C bricks with neither significant alteration nor infiltration of alien components, and the remaining of large magnesite crystal grains in high grade fused magnesite particles can be observed.

The physical and chemical properties of recycled MgO-C raw materials compared with original fused magnesite raw material are shown in Table 1. The recycled raw material is composed mainly of magnesite and carbon at a composition close to the average C content in MgO-C brick relined in converter furnaces. The high apparent porosity of recycled raw material is attributable to the existence of pores contained in MgO-C aggregate particles, one of the major components in the recycled MgO-C brick raw material.

3. MgO-C Green Refractories Blended with Recycled Raw Materials

The typical physical and chemical data of two

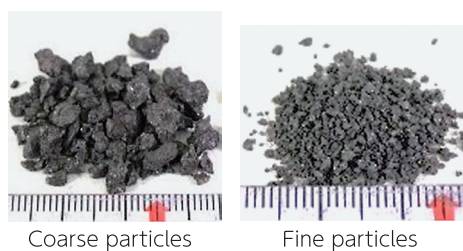


Fig. 2 Exterior appearance of recycled raw materials.

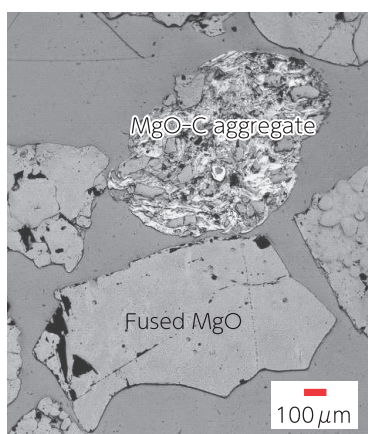


Fig. 3 Microscopic photograph of recycled raw material.

Table 1 Physical and chemical properties of recycled MgO-C raw materials and fused MgO

Physical properties		
	Recycled raw material	Fused MgO
Apparent porosity / %	8.2	0.6
Bulk density / -	3.03	3.56
Apparent density / -	3.30	3.58
Chemical composition / %		
MgO	78.9	97.6
CaO	1.3	1.8
SiO ₂	1.0	0.5
Fe ₂ O ₃	0.5	0.3
Free C	15.6	<0.1

をTable 1に示す。比較には、一般グレードで使用される高純度電融マグネシアの値を併せて示した。リサイクル原料は、成分としてマグネシアとカーボンを主体とし、カーボンの値は平均的な転炉用MgO-Cれんがに近い値を示した。リサイクル原料の見掛け気孔率が高いことは、使用済みMgO-Cれんが組織の一部であった複合粒子集合体に一定の気孔が含まれるためであると考えられる。

3. リサイクル原料含有MgO-Cれんが (Green refractory)

リサイクル原料を使用したMgO-Cれんがの物理特性、化学組成および耐食性指数を転炉用汎用グレードのMgO-Cれんが(C=15%品)と比較し、Table 2に示す。ここで、MgO-Cれんが中のリサイクル原料の使用率を20%、40%としたものをR20、R40と表記する。アーク加熱式回転炉内張法による侵食試験後の溶損量を、従来品を100に換算し、溶損指数として示した。侵食試験の試験温度は1700℃、試験時間は5時間とした。スラグはC/S=3の合成スラグを使用した。

従来品と比較して、R20、R40の見掛け気孔率はやや高く、かさ比重はやや低い。これはリサイクル原料が高気孔率であることに由来し、使用量に依存される。次に、R20の化学組成は従来品と同等、R40ではフリーカーボン値の上昇がみられた。R20の溶損指数は、従来品と略同等、R40の溶損指数は約10%大きい。物理特性と溶損指数から、R20

types of MgO-C Green Refractories containing recycled raw materials are compared with ordinary MgO-C brick with 15 % carbon content which is commonly applied as relining material for converter furnace are shown in Table 2. R20 and R40 of MgO-C Green Refractories are named after the 20 % and 40 % blending ratio of recycled raw materials, respectively. In comparison with ordinary MgO-C brick, R20 and R40 of MgO-C Green Refractories exhibit slightly higher apparent porosity and slightly lower bulk density, both of which are attributable to the blending of recycled raw materials. The degree of alternation corresponds with the blend composition of recycled raw materials. R20 MgO-C Green Refractory brick exhibits the almost similar chemical compositions. The free carbon content of R40 MgO-C Green Refractory brick is slightly higher than that of ordinary and R20 MgO-C brick.

To evaluate the corrosion resistance of three kinds of MgO-C brick, rotary drum corrosion test with arc heating was conducted at 1700 °C for 5 hours with synthetic slag of 3.0 of basicity (C/S) as the corrosive agent. The corrosion test results were compared with a wear index of 100 representing the corroded volume of an ordinary Mg-C brick sample specimen. R20 MgO-C Green Refractory brick exhibited almost an equivalent level of wear index to that of ordinary MgO-C brick, while the wear index of R40 MgO-C Green Refractory brick deteriorated by roughly 10 %.

The analyzed physical properties and corrosion test results in for that R20 MgO-C Green Refractory brick is applicable for the metal bath layer in converter furnaces, and R40 MgO-C Green Refractory brick could be used to reline positions where corrosive damage is not so severe, such as the throttling part of the converter furnace. Needless to mention, MgO-C Green Refractories can be applied to furnaces or vessels other than converter furnaces, such as electric furnaces or teeming ladles.

4. Estimate on Reduction of CO₂ Gas Emission Volume

The amount of energy consumption required for the production of refractory bricks depends on the type of bricks. Among them, MgO-C brick is a typical unfired product with low energy consumption in

Table 2 Typical physical and chemical data of ordinary MgO-C and two types of MgO-C Green Refractories

	Ordinary (C=15%)	Containing recycled raw material	
		R20	R40
Physical properties			
Apparent porosity / %	3.5	4.3	5.8
Bulk density / -	2.94	2.92	2.89
Cold crushing strength / MPa	35	32	20
Chemical composition			
MgO / %	78	78	76
CaO	1	1	1
Free C	15	15	17
Slag corrosion resistance			
Wear index*	100	103	112

*The smaller index is better.

は転炉鋼浴部に、R40は比較的損傷の軽微な非激食部や裏張りなどへの適用が可能と考える。転炉以外にも、電気炉や溶鋼鍋等に広く適用できる可能性がある。

4. CO₂排出量の試算

MgO-Cれんがは不焼成れんがであることから、れんが製造に必要な消費エネルギーのほとんどは主原料である電融マグネシア原料製造時のエネルギーに由来するところが多い。そこで、従来材、R20、R40のMgO-Cれんが1トンに使用する原料製造に由来するCO₂排出量を見積もり、比較した。その結果をFig.4に示す。電力使用量は太田⁶⁾や野田⁷⁾、原料メーカーへのヒアリングなどを元に推定

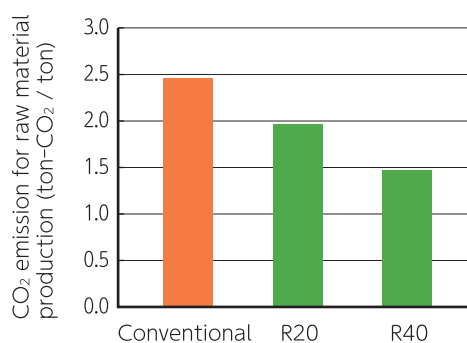


Fig. 4 Estimated CO₂ gas emission volume generated for production of MgO-C bricks.

the manufacturing process. However, since high purity electro-fused magnesia is used as the main raw material, the energy consumption during raw material production accounts for a large proportion of the energy consumption throughout the life cycle of MgO-C brick products and has a significant impact on CO₂ gas emissions. Therefore, we estimated the amount of CO₂ gas emissions required to produce one ton of MgO-C Green Refractory R20 and R40 with different recycled MgO-C raw material contents, and compared them with a conventional material produced only with virgin raw materials. The electric power consumption corresponding to the energy consumption demanded for electro-fused magnesia production was determined by referring to references by Ohta⁶⁾ or Noda⁷⁾ as well as interviews with refractory raw materials suppliers and was used in the calculations. The emission factor used in electric power industry in Japan was adopted for converting electric power to CO₂ gas emission volume. As per Fig. 4, in which estimates of CO₂ gas emission volume generated for production of these three types of MgO-C brick are compared, 0.5 tons and 1.0 tons of CO₂ gas emission volume can be reduced by replacing the conventional MgO-C brick with R20 and R40 of MgO-C Green Refractory brick, respectively.

し、日本国内における電気事業者排出係数を使用して算出した。CO₂排出量は、従来材に対してR20で0.5t-CO₂/トン、R40で1t-CO₂/トン削減できると見積もられた。

5. 結言

MgO-Cれんがのリサイクル用途の拡大を目的に、転炉で内張りされた高グレード使用済みMgO-Cれんがを原料として再資源化するプロセスを確立し、得られたリサイクル原料を使用した“Green Refractory”に該当するMgO-Cれんがを開発した。当れんがの各種炉への適用、拡大により原料製造時のCO₂排出量削減効果が期待できる。

5. Conclusion

For the purpose of scaling up recycling application of used MgO-C bricks, the recycling process of used high-grade MgO-C bricks relined in the converter furnace has established. MgO-C Green Refractories were developed by blending in over 20 % recycled raw materials. , A large reduction of CO₂ gas emission volume is expected with increased applications of MgO-C Green Refractories in various types of furnaces or vessels.

References

- 1) S. Hanagiri et al.: Shinnittetsu giho, 388 93-98 (2008).
- 2) S. Takashima et al.: Nippon Seitetsu giho, 415 70-74 (2020).
- 3) A. Harada: Taikabutsu, **75** [9] 399-402 (2023).
- 4) Tae hwa Lee et al.: UNITECR 2023 proceedings.
- 5) T. Shiotani et al.: Taikabutsu, **66** [7] 312-316 (2014).
- 6) T. Ohta: Nishiyama Seminar Memorial 48th and 49th, Tokyo, ISIJ, 21-23 (1977).
- 7) I. Noda et al.: Journal of the Society of Chemical Industry, Japan, **59** [11] 1330-1334 (1956).