[Technical Report]

MgO-CaO 系電気炉吹付材の開発

Development of MgO-CaO repairing materials for EAF

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１　緒言

製鋼用電気炉では不定形材料の補修を前提とした操業が行われている。特に，操業間や稼働後の休止時には大量の吹付補修材が使用されており，使用する吹付材の良否が電気炉製鋼の操業や経済性に大きく影響を与える1)。従来より，電気炉の吹付補修においては耐食性やコスト面などから MgO 系 ,MgO-Olivine 系吹付材が一般的に使用されているが，塩基性で高耐用性として知られる MgO-CaO 系吹付材は使用されることは少ない2-6)。MgO-CaO 系吹付材は，耐火物中に含有する CaO により耐スラグ浸潤性に優れ，高い耐食性を示す一方で，製品の品質安定性の面から焼成ドロマイト若しくは合成ドロマイトと呼ばれる CaO を安定化した加工ドロマイト原料を使用しなければならず，通常の焼成マグネシアのみの吹付材と比較すると製品コストが比較的高くなる傾向にある。そのため，コスト面を考慮すると電気炉吹付材には適用しにくく一般的に展開されてこなかった。また，稼働・休止を繰り返す電気炉操業においては，材料中に含まれるフリーライムの消化現象により吹付け後の施工体組織が劣化する現象も想定され技術的な面でも適用のし難さがある。

今回，これらのコスト面・技術面の課題を解決する為，天然の非焼成ドロマイトである苦土石灰石の使用を検討し，MgO-CaO 系吹付材の耐食性の良さを活かした新規の吹付材の開発を試みた。

２　試験方法

２・１　供試試料

試験に用いた塩基性吹付材は珪酸塩をボンドとした MgO=88 mass% の材料をベース試料とした。ベース試料中の焼成マグネシアを苦土石灰石に 10，20，40mass% 置換し，併せて，焼結助剤として SiO_2 系

1 Introduction

In the electric arc furnace for steelmaking, the operation is carried out assuming the repair by the monolithic material. In particular, a large amount of gunning repairing material is used during operation and during shutdown after operation, and the quality of the gunning repairing material greatly affects the operation and economical efficiency of electric arc furnace steelmaking1). MgO and MgO-Olivine gunning repairing materials have been commonly used for repair of electric arc furnaces for cost performance, but MgO-CaO gunning repairing materials, which are known to have high corrosion resistance, are rarely used2-6). The MgO-CaO gunning repairing material has excellent slag infiltration resistance and high corrosion resistance due to CaO contained in refractory. On the other hand, from the viewpoint of product quality stability, CaO-stabilized dolomite raw materials called calcined dolomite or synthetic dolomite must be used, and the product price tends to be comparatively higher than the gunning repairing material of usual calcined magnesia only. Therefore, it is difficult to apply it to electric arc furnace gunning repairing material, considering the cost, and it has not been developed generally. And, in the electric arc furnace operation which repeats operation and shutdown, the phenomenon in which the construction body after gunning deteriorates by the digestion phenomenon of free lime included in the material is also assumed, and there is a difficulty in the application even in the technical aspect.

In order to solve these cost and technical issues, we examined the use of natural non-calcined dolomite and tried to develop a new gunning repairing material utilizing the good corrosion resistance of MgO-CaO based gunning material.

2 Laboratory test

2・1 Test sample

The basic gunning repairing material used in the test was a material with MgO = 88 mass% using silicate as a binder, and this was used as a base sample. Calcined magnesia in the base sample was substituted with non-

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Table 1 Composition of samples.

Sample		No.1	No.2	No.3	No.4
Material composition / mass%	Magnesia 5-0mm	95	85	75	55
	Dolomite 5-0mm	0	10	20	40
	Binder+Other	5	5	5	5
	Sintering agent	-	1.5	1.5	1.5
Chemical composition / mass%	MgO	88	81	74	60
	CaO	1	4	8	14

添加剤，その他微量のバインダーを外掛けで加えた系を供試試料とした。**表 1** に各試料の苦土石灰石の添加量，化学成分を示す。

２・２　一般物性

各試料について混練，鋳込み成型したものを 110℃で 24 時間乾燥後，1400℃で 3 時間の酸化焼成を行った。脱枠時の試料寸法と 1400℃焼成後の試料寸法から残存線変化率を算出し，3 点曲げ試験により曲げ強さを測定し，真空法により見掛気孔率を測定した。

２・３　鉱物組成調査

2･2 と同様の手順で 110℃乾燥後試料並びに 1000℃，1400℃で 3 時間焼成した試料を作製し，それぞれ粉砕した後，粉末 X 線回折（XRD）より，鉱物組成の変化を調査した。

２・４　耐食性

各試料の耐食性を評価する為，回転ドラムを用いて回転侵食試験を行った。2･2 と同様の手順で各試料を所定の形状に成型し，侵食試験用試料とした。作製試料を回転ドラム内にセットし，**表 2** に示す電気炉スラグを模した C/S=1.0 の合成スラグを侵食剤として，1650℃で 4 時間侵食試験をした。試験後，試料の稼働面を中央で切断し，切断面にて試料の厚みを 5 点計測平均し，試験前試料寸法との差で溶損・消失した厚みを算出した。スラグ浸潤厚みは黒色変色部位 5 点を計測し平均して算出した。

calcined dolomite by 10, 20 and 40 mass%. In addition, a system in which SiO_2 additives and a small amount of other binders were added as sintering additives was used as a test sample. **Table 1** shows the amount of non-calcined dolomite added and the chemical composition of each sample.

2・2 Physical properties

The kneaded and cast samples were dried at 110℃ for 24 h and then oxidized at 1400℃ for 3 h. The permanent linear change rate was calculated from the sample size in the frame removal and the sample size after baking at 1400℃, and the bending strength was measured by a 3-point bending test, and the apparent porosity was measured by a vacuum method.

2・3 Mineral composition survey

Samples dried at 110℃ and samples fired at 1000℃and 1400℃ for 3 hours were pulverized by the same method as that used in 2・2, and changes in mineral composition were investigated by X-ray diffractometer (XRD).

2・4 Corrosion resistance

In order to evaluate the corrosion resistance of each sample, erosion tests were carried out using a rotating drum. Each sample was molded into a prescribed shape by the same procedure as 2・2, and used as a sample for erosion test. The prepared samples were set in a rotating drum, and a synthetic slag of C/S = 1.0 simulating electric arc furnace slag shown in **Table 2** was used as an erosion agent, and erosion tests were carried out at 1650℃ for 4 hours. After the test, the working surface of the sample was cut in the center, and the thickness of the sample was measured and averaged at the cutting surface by 5 points, and the thickness which melted and disappeared by the difference from the sample size before the test was

Table 2 Chemical composition of slag. / mass%

SiO_2	Al_2O_3	Fe_2O_3	MnO	CaO	MgO	C/S
27.5	5	30	5	27.5	5	1.0

Table 3 Condition for gunning.

Gunning machine	Brader gun
Air pressure	0.14 MPa
Nozzle length	800mm (straight)

２・５　熱間吹付け試験

各試料の熱間での付着性を評価する為，1000℃に加熱したパネルへの吹付け試験を行った。その他の吹付け条件については**表3**に示す。吹付け後，パネルに付着せず落下した材料を回収・乾燥し，吹付けした全体量に対する割合を算出し，付着率を求めた。

３　結果と考察

３・１　一般物性

1400℃焼成後試料の曲げ強さ及び残存線変化率、見掛気孔率を**図1～3**に示す。

calculated. The thickness of slag infiltration was calculated by measuring 5 points of black discoloration and averaging them.

2・5 Hot panel gunning test

In order to evaluate the hot adhesiveness of each sample, gunning tests were carried out on a panel heated to 1000℃. Other gunning conditions are shown in **Table 3**. After gunning, the material dropped without adhering to the panel was collected, dried, and the ratio to the total amount gunned was calculated to obtain the adhesion ratio.

3 Results and discussion

3・1 Physical properties

The bending strength, permanent linear change rate and apparent porosity of the sample after firing at 1400℃ are shown in **Fig. 1 ~ 3**.

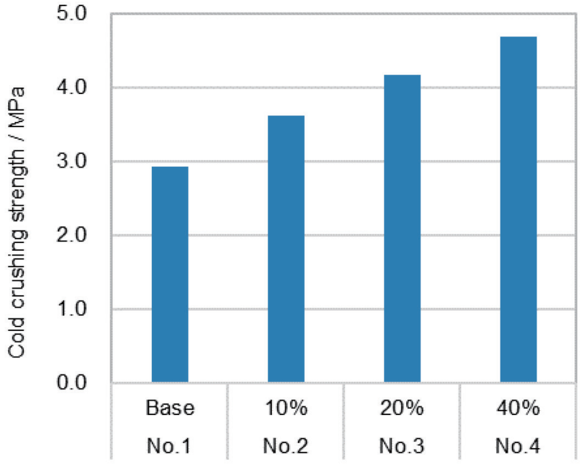

Fig.1 **Cold crushing strength after firing at 1400℃ for 3hours.**

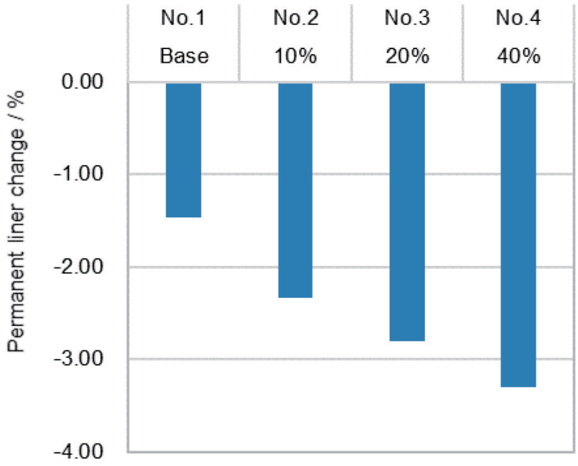

Fig.2 **Permanent liner change after firing at 1400℃ for 3hours.**

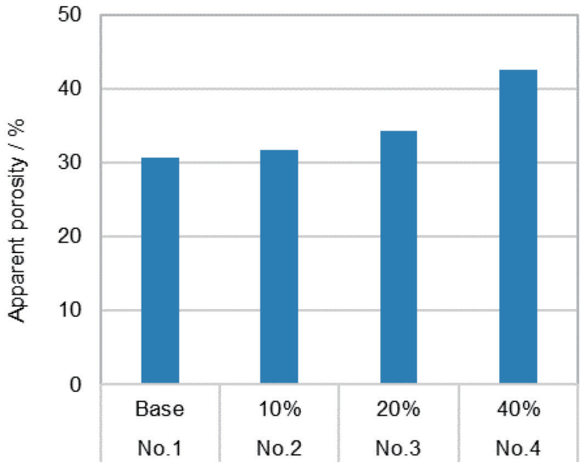

Fig.3 **Apparent porosity after firing at 1400℃ for 3hours.**

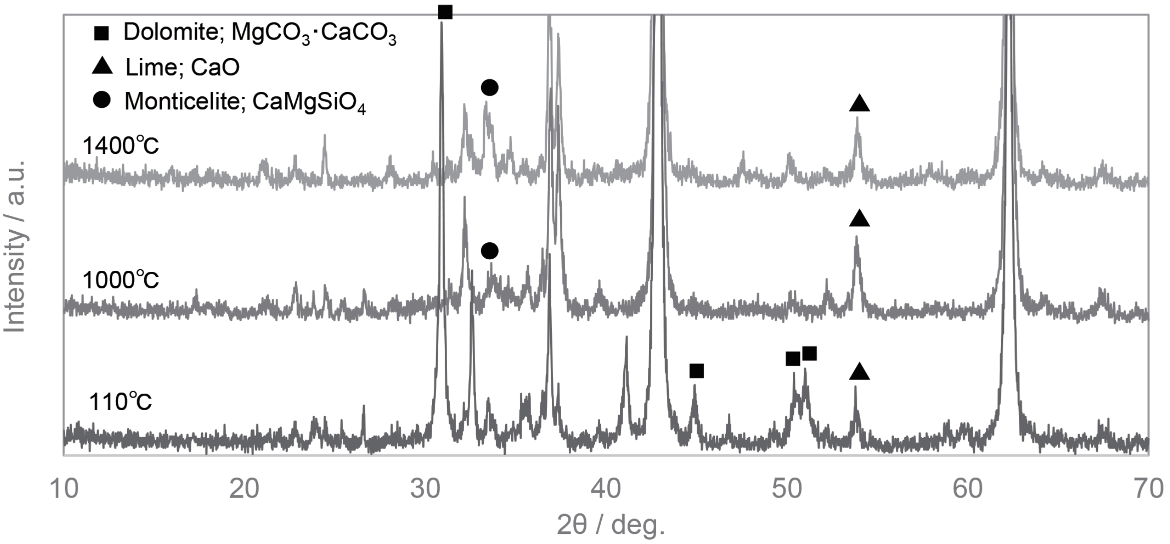

Fig.4 X-ray diffraction patterns of sample No.4

苦土石灰石の適用量が多くなる程，焼成後の曲げ強さが大きくなる結果となった。また，焼成後収縮は大きくなり，見掛気孔率は増加する結果となった。苦土石灰石の添加により，各種物性に顕著に影響を及ぼすことが判明した。これらの反応メカニズムを明らかにする為，苦土石灰石の適用量が最も多い No.4 を選定し，110℃乾燥品，1000℃，1400℃焼成品について粉末 X 線回折（XRD）により，鉱物組成の変化を調査した。加熱処理後の各試料の測定結果を**図 4** に示す。

図 4 より，110℃においては苦土石灰石の主要成分である Dolomite（$MgCO_3$・$CaCO_3$）のピークが明瞭に確認できる。1000℃では，Dolomite（$MgCO_3$・$CaCO_3$）のピークが消失している一方で，分解生成物であるフリーライム（CaO）のピークが認められることから，分解反応が進行していることが確認できる。1400℃に至るとフリーライム（CaO）のピークが低下し，CaO-MgO-SiO_2 系鉱物である Monticellite（$CaMgSiO_4$）のピークが大きくなり，焼結反応が進んでいることがうかがえる。苦土石灰石を添加することで，1000℃以上で Dolomite（$MgCO_3$・$CaCO_3$）の分解生成物であるフリーライム（CaO）と MgO-SiO_2 系鉱物との反応を経て Monticellite（$CaMgSiO_4$）が生成・焼結し，高強度化並びに収縮が生じたと推察する。

The higher the amount of non-calcined dolomite applied, the greater the bending strength after firing. The shrinkage increased and apparent porosity increased after firing. It was found that the addition of non-calcined dolomite significantly affected the properties of each species. In order to clarify these reaction mechanisms, No.4, in which non-calcined dolomite was most applied, was selected, and the change of mineral composition was investigated on the products dried at 110℃ and baked at 1000℃ and 1400℃ by powder X-ray diffractometer (XRD). The measurement results of each sample after the heat treatment are shown in **Fig. 4**.

From **Fig. 4**, at 110℃., the peak of Dolomite ($MgCO_3/CaCO_3$), which is the main component of non-calcined dolomite, can be clearly observed. At 1000℃, the peak of Dolomite ($MgCO_3/CaCO_3$) disappeared, while the peak of free lime (CaO), a degradation product, was observed. At 1400℃, the peak of free lime (CaO) decreased and that of Monticellite ($CaMgSiO_4$), a CaO-MgO-SiO_2 mineral, increased, suggesting that the sintering reaction proceeded. By the addition of non-calcined dolomite, Monticellite ($CaMgSiO_4$) was formed and sintered through the reaction of free lime(CaO) which is the decomposition product of Dolomite ($MgCO_3/CaCO_3$) with MgO-SiO_2 system mineral at over 1000℃, and it was estimated that strengthening and shrinkage occurred.

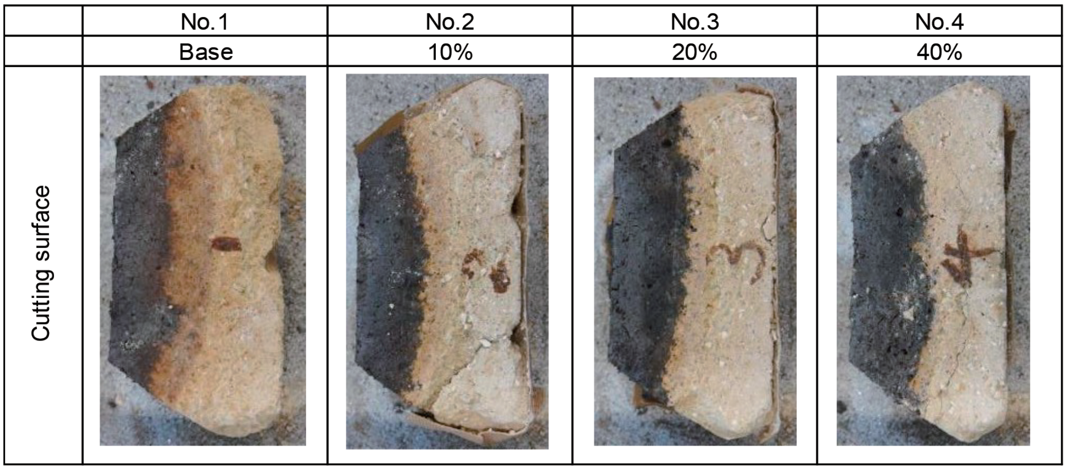

Fig.5　Appearance of cutting surface after corrosion test

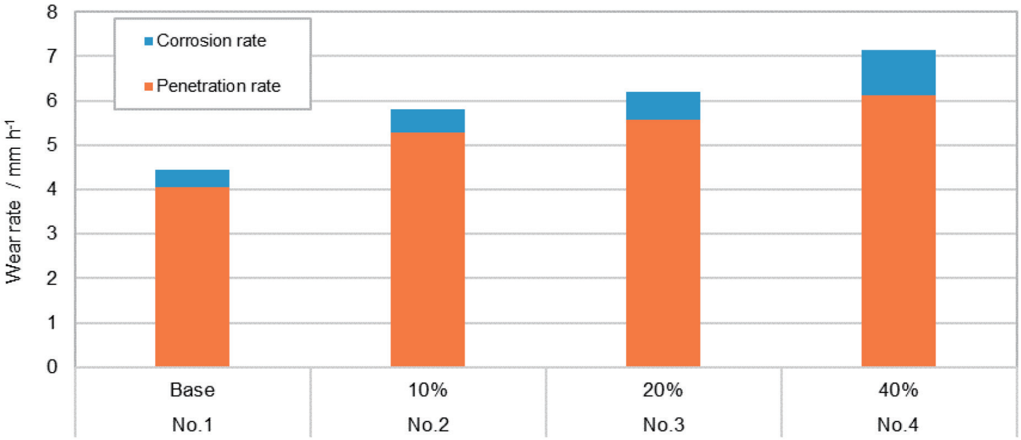

Fig.6　Results of corrosion test.

３・２　耐食性

回転侵食試験後試料の外観を**図 5**，溶損量並びにスラグ浸潤速度を**図 6** に示す。

苦土石灰石の添加量が増えると，溶損量，スラグ浸潤量共に微増する傾向となったものの，1 時間当たりの溶損量と浸潤量の合計増加量は No.2 ～ No.4 のいずれの試料も 3mm 以下となり，大きな耐食性の低下は認められなかった。苦土石灰石を添加することで，加熱により材料中に CaO が生成し，スラグ浸潤抑制効果が発現する一方で，苦土石灰石の脱ガス分解反応により，稼働面での比表面積の増加と材料内部へ通じる開放気孔が増えることで No.1 ベース試料よりも溶損量，スラグ浸潤量が増えたものと推察する。

3・2 Corrosion resistance

Fig. 5 shows the appearance of the sample after erosion test, and **Fig. 6** shows the amount of disappearance and slag infiltration.

As the amount of non-calcined dolomite added increased, both the amount of erosion and the amount of slag infiltration slightly increased. However, the total amount of erosion and the amount of infiltration per hour was less than 3 mm in all the samples from No. 2 to No. 4, and there was no significant decrease in corrosion resistance. By adding non-calcined dolomite, CaO is generated in the material by heating, and the slag infiltration depression effect appears, and it is guessed that by the degassing decomposition reaction of non-calcined dolomite, the erosion loss quantity and slag infiltration quantity increased more than the No.1 base sample by the increase of specific surface area in the working surface and the increase of open pores to the material inside.

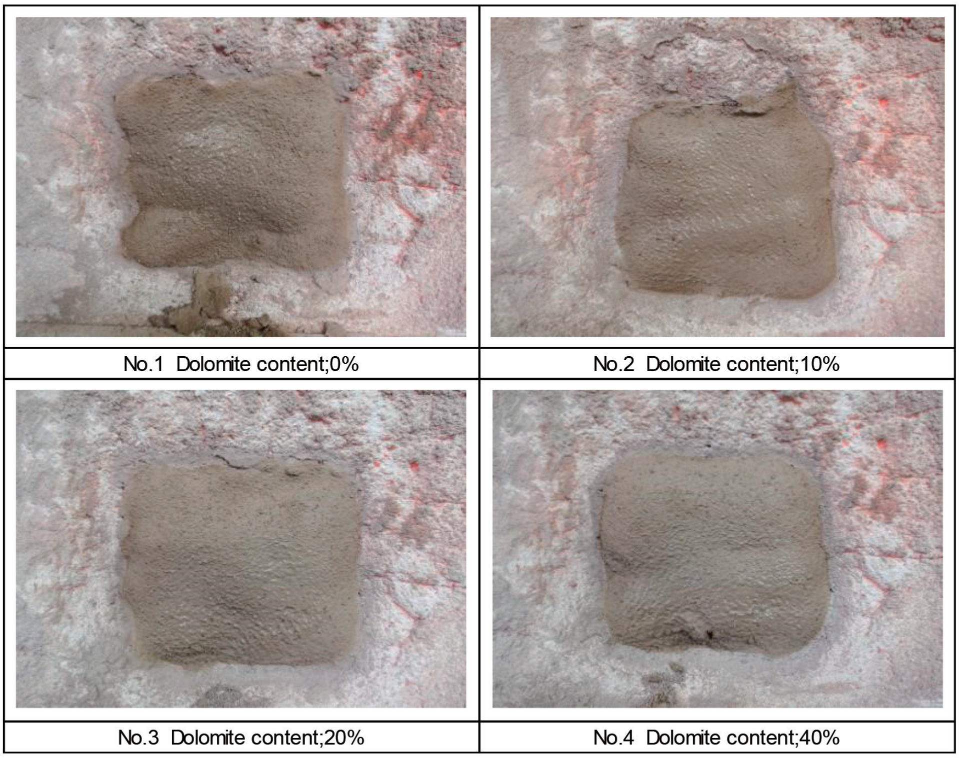
No.1 Dolomite content;0%
No.2 Dolomite content;10%
No.3 Dolomite content;20%
No.4 Dolomite content;40%

Fig.7 Appearance after gunning test.

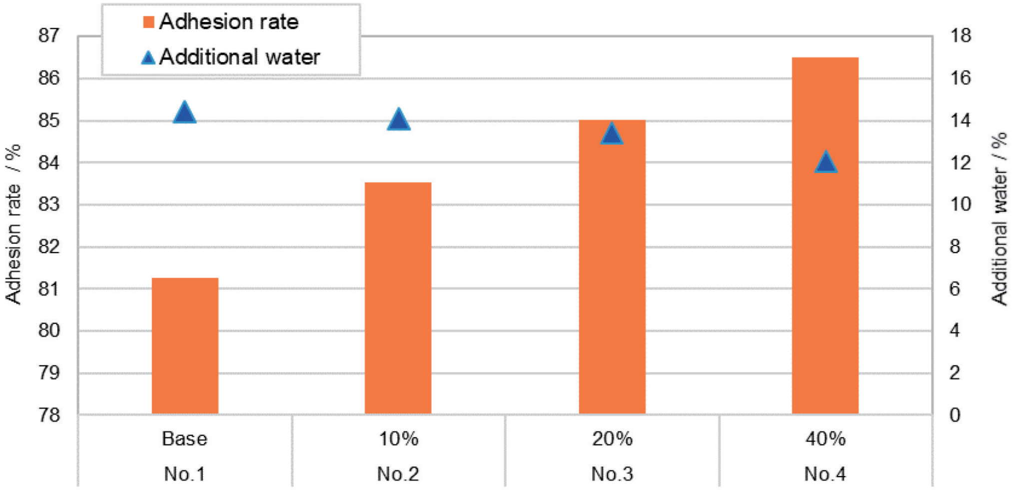

Fig.8 Results of the adhesion rate and additional water in hot gunning test.

３・３　熱間吹付け試験

熱間吹付け後の施工体外観を**図 7**，吹付け水分と付着率を**図 8** に示す。

試験結果より，苦土石灰石の添加量が増えるに従い，吹付け水分量が低下する傾向にあった。また，付着性も向上する傾向にあることが判った。苦土石灰石は焼成マグネシアよりも見掛気孔率が低いため，置

3・3 Hot panel gunning test

Fig. 7 shows the appearance of the sample after hot gunning, and **Fig. 8** shows the amount of added water and adhesion rate.

The test results showed that the added water content tended to decrease as the amount of non-calcined dolomite in the gunning repairing material increased. And, it was proven that the adhesion tended to improve. Since the apparent porosity of non-calcined dolomite is lower than that of fired magnesia, it is considered that the

Table 4 Effects of adding non-calcined dolomite to repairing materials for EAF.

Characteristics		Dolomite effects (vs MgO system)
Physical properties	Cold crushing strength	↗ Improve
	Permanent liner change	↘ Shrink
	Apparent porosity	↘ Increase
Durability	Corrosion resistance	↘ Decrease
Workability	Adhesion	↗ Improve
Other	Digestibility	None

換により骨材の気孔に吸われる水分量が減り，材料全体が混水するのに必要な水分量が減少したためと考える。また，水分量が低下することで吹付材中の相対的なバインダー濃度が高まり，凝集作用が強まることで付着性が向上したと考える。

３・４　苦土石灰石の添加効果

ラボ試験結果より，MgO 質吹付材への苦土石灰石の添加は各種性質に対して一長一短の影響があることが認められた。以下，**表 4** に内容をまとめた。

苦土石灰石の添加により，見掛気孔率の増加，スラグに対する溶損量は増加するが，熱間付着性，材料強度は MgO 質吹付材よりも向上する結果となった。付着性の向上は結果的に吹付材全体の耐用性に関わり，強度の向上は剥離損耗に対して抵抗性が増す。苦土石灰石の添加は，吹付材の総合的な性能に対してメリットがあり得ると考えられる。

４　実炉試験

ラボ試験にて検討した No.3 材質を溶解～出湯サイクル１時間で出湯温度 1600 ～ 1630℃，スラグ C/S=1.0 程度である製鋼用電気炉にて耐用性評価をした。評価手法として，吹付材を約 100t 連続使用し，その際の原単位と原単価を指数化した。その結果を**図 9**, **図 10** に示す。

従来の当社製品（No.1;MgO 系）に対して，No.3 材質は同等レベルの原単位となり，原単価比較では 13% の削減効果が認められた。加えて，ドロマイト系吹付材は通常，吹付け後に施工体が消化する作用が知られているが，今回実炉にて試験した No.3 材質では吹付け後の消化現象は認められず，施工体の亀裂・剥離も認められなかった。

苦土石灰石を適用した吹付材は，MgO 系材質に

substitution decreases the amount of water absorbed in the pores of the aggregate and decreases the amount of water required for mixing the whole material. In addition, it is considered that the relative binder concentration in the gunning repairing material was increased by the decrease of the water content, and the cohesion was strengthened, and the adhesion was improved.

3・4 Effect of non-calcined dolomite addition

From the laboratory test results, it was recognized that the addition of non-calcined dolomite to MgO gunning repairing material had advantages and disadvantages for various properties. The contents are summarized in **Table 4**.

The addition of non-calcined dolomite increased the apparent porosity and the amount of melting loss to slag, but improved the hot adhesion and the material strength compared with the MgO gunning repairing material. The improvement of the adhesiveness is related to the durability of the whole gunning repairing material as a result, and the improvement of the strength increases the resistance for the peeling wear. The addition of non-calcined dolomite is considered to be beneficial for the overall performance of gunning repairing materials.

4 Actual furnace test

The durability of No.3 material examined in laboratory tests was evaluated in an electric arc furnace for steelmaking in which the tapping temperature was 1600 ~ 1630℃ and the slag C/S was about 1.0 in 1 hour of the melting to tapping cycle. As an evaluation method, the gunning repairing material was continuously used about 100 t, and refractory consumption and cost in that time were made to be an index. The results are shown in **Fig. 9** and **10**.

Compared with the conventional our company products (No. 1; MgO system), the consumption of the No.3 material was equivalent, and 13% reduction effect was recognized in cost comparison. In addition, it is known that the dolomite gunning repairing material is usually digested by the construction body after gunning, but the digestion phenomenon after gunning was not observed in No.3 material tested in the actual furnace this

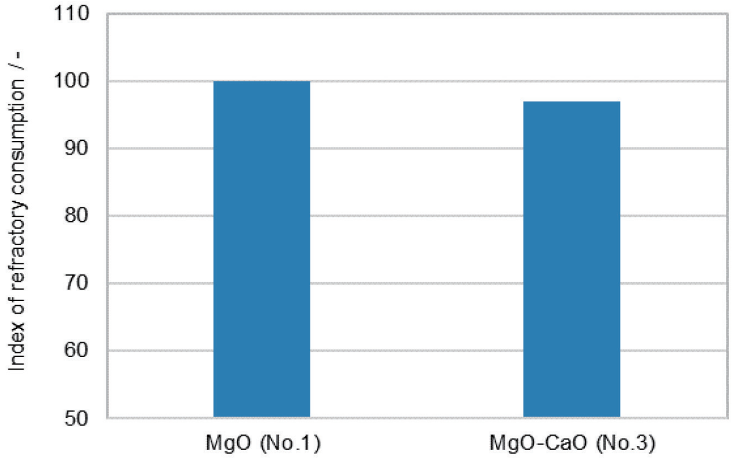

Fig.9　Field test results (Index of refractory consumption).

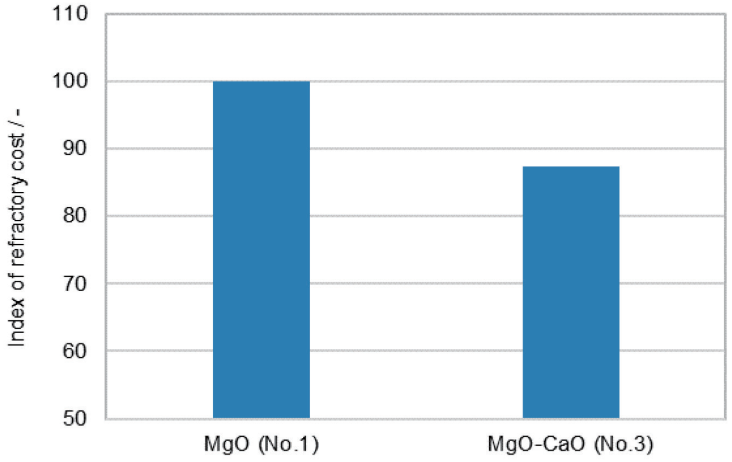

Fig.10　Field test results (Index of refractory cost).

比較して溶損量が若干増えるものの，一方で，吹付け時のリバウンドロス低減効果により施工体厚みが増し，施工体の残存性に対してプラスに働く。また，苦土石灰石の焼結性により施工体強度が向上する為，溶鋼・スラグ衝撃に対する抵抗性が増し，剥離損耗が抑えられる。これらの点がMgO系材質と同等レベルの原単位になった理由と推定される。今回試験をした電気炉の操業条件下では良好な結果となったが，溶損がより助長される条件，例えば，溶解時間が長時間であることや出湯温度が1650℃を大きく超える条件下では今回開発した苦土石灰石添加吹付材での高耐用性は期待し難いと考える。現状はユーザー毎の施工条件・操業条件を加味した上で本吹付材の提案をしている。

time, and cracks and peeling of the construction body were not observed.

The gunning repairing material to which the non-calcined dolomite is applied has a little more erosion quantity than the MgO system material, but on the other hand, the thickness of the work increases by the rebound loss reduction effect in gunning, and it works positively for the persistence of the work. And, the resistance against molten steel and slag impact increases, and peeling loss is suppressed, since the strength of construction body is improved by the sinterability of non-calcined dolomite. These points are estimated to be the reason why the refractory consumption became equivalent to the MgO system material. Although the results were good under the operating conditions of the present electric arc furnace, the high durability of the newly developed non-calcined dolomite addition gunning repairing material is not expected under the conditions that the erosion is promoted

５　まとめ

苦土石灰石を使用することで，MgO系等の従来材質よりもコストパフォーマンスに優れる新規のMgO-CaO系吹付材の開発をした。その優れた特性より，国内外の電気炉メーカーに評価して頂き，今日現在既に７社以上で定常的に使用して頂いている。また，新規に実炉での評価を予定して頂いているメーカーも数社あり，今後，MgO-CaO系吹付材が一般的なものとして認知されていくことを期待している。本報告では電気炉での使用結果を報告したが，苦土石灰石を適用した吹付材は電気炉向けの用途だけではなく，製鋼プロセスにおける各種窯炉のオンライン補修やその材料安定性からオフライン補修にも適用できると想定され，現在，転炉や二次精錬用熱間吹付材への展開も視野に開発を進めている。

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本論文は以下の報文を翻訳・加筆・再構成して転載したものである。
大野他：耐火物, **73** [2] 38-44 (2021).

more, for example, the melting time is long and the tapping temperature is over 1650℃. At present, this gunning repairing material is proposed after considering the construction and operation conditions of each user.

5 Summary

By using natural non-calcined dolomite, we have developed a new MgO-CaO gunning repairing material that is superior in cost performance to conventional materials such as MgO. Due to its excellent characteristics, it has been well received by electric arc furnace manufacturers in Japan and overseas, and it has been used regularly by over 7 companies at present. In addition, several manufacturers are planning to conduct tests in actual furnaces, and it is expected that MgO-CaO based gunning repairing materials will be widely recognized in the future. In this report, the result of the use in the electric arc furnace is reported, and it is assumed that the gunning repairing material which applied the non-calcined dolomite can be applied not only to the electric arc furnace but also to on-line repair and off-line repair of various furnaces in the steelmaking process. At present, the development of gunning repairing material for converter and secondary refining is advanced.

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This paper is translated and reprinted with some additions and reconstructions to the following paper:
Yousuke Oono et al.: *Taikabutsu*, **73** [2] 38-44 (2021).