

SHINAGAWA TECHNICAL REPORT

高炉の安定操業および低CO₂排出に貢献する グラフェン状構造を持つマッド材

Graphene-like Structured Tap Hole Clay for Stable Blast-furnace Drainage and Lower CO₂ Emissions

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報文／REPORT

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要 旨

安定した高炉操業は、マッド材の性能が大きく影響する。マッド材は、スラグによる溶損と銑鉄による侵食が複合的に作用し損傷する。このような背景のもと、鉄鋼生産における低品質原料の使用や高炉操業の低コスト化によって操業条件が厳しくなっているが、グラフェン状構造を持つ革新的なマッド材を使用することでそれらの問題を解決した。化学的な損傷に対する耐性に優れることで安定した炉内堆積基盤の形成と出銑流を実現するこの技術は、高炉の低燃費操業を可能にし、製鉄分野におけるCO₂排出量と耐火物使用量の削減に貢献している。

Abstract

A stable blast-furnace operation is strongly associated with the performance of tap hole clay, which is usually damaged by the combined effect of slag corrosion and pig iron erosion. As such scenario has recently become more challenging for the steel producers due to the use of lower quality raw-materials and lower cost operational practices, Shinagawa Refractories Brazil developed a high-performance solution based on an innovative tap hole clay with a graphene-like structure. Owing to an outstanding chemical resistance and, consequently, a stable mushroom and metal flow, such technology allows operations with reduced fuel consumption, helping to reduce the CO₂ emissions and the refractory usage in the ironmaking area.

1. 緒言

高炉操業は、製鉄所全体の生産性を決定する、銑鋼一貫製鉄の重要な工程である。低出銑操業あるいは不安定状態の高炉は、非稼働の混銑車数の増加や、鋼材加熱頻度の増加に伴うエネルギーの消費、更には重要な最終製品の歩留まり低下など、様々な悪影響を招く。

1. Introduction

The blast-furnace operation is a key step in the steel production chain, as it defines the productivity level of the whole mill. A blast-furnace running with low production level or under unstable conditions will lead to a series of undesired consequences, such

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高生産性操業を妨げる要因は数多くあるが、最も懸念される要因の一つはメタルとスラグの非効率的な排出であり、これが高炉の液面を上昇させ、送風圧力が不安定になり負荷が低下することである¹⁾。出銑孔の侵食量は排出されるスラグとメタルの流量に影響するため、マッド材は重要な役割を持つ。北村ら²⁾とYounら³⁾は、様々なマッド材を評価し、耐食性を向上させる最適な組み合わせを示した。

マッド材は、メタルとスラグを適切に排出する以外に、出銑孔近傍の炉壁を保護するために、深度が長くて強固な炉内堆積基盤を形成し維持する働きもある⁴⁾。土屋ら⁵⁾は、高炉の使用後解析を行い、出銑孔深度が炉芯の位置によって変化し、炉内堆積基盤の安定性に影響を及ぼす可能性がある⁶⁾と結論づけた。

その上、高炉操業で適用される最近のコスト削減手法は、メタルの環状流の変化やスラグの化学的変化の活性により標準的な炉内条件に大きな影響を及ぼしている^{4),6)}。市場における一般的なマッド材は、この20年間に於いて画期的な技術が芽生えなかったことで、悪条件下で性能を発揮することに苦労してきた。

そのような停滞状態において、2017年、Sakoらは最適粒度と非常に高性能な解膠剤を組み合わせ、適度な塑性挙動と優れた接着性を両立した新技術を開発した⁷⁾。この発想の背景には、溶銑の差し込みや閉塞不良を起こすことなく出銑孔を適切に閉塞でき、炉壁と既存の堆積基盤に強固に接着するマッド材を供給することにある。この技術は、炉壁保護の有力な手段ではあったものの、耐食性に課題が残されていた。

しかしながら、一般的に主なマッド材の添加物はコークス、ピッチ、タール、カーボンブラックであり、これらは非晶質相のみで構成され、黒鉛化しにくい。すなわち、これらは強靱で濡れにくい微構造の生成に至らないため、昨今のマッド材は上述のような一般的な性能に留まっている。

最先端の炉床壁保護の基本的な思想を補完した最高のマッド材技術に到達するために、耐食性の革新的な解決手法としてグラフェン状構造に着目した。グラフェンは、利用可能な究極の二次元材料として世界的に有名で、1原子の厚さのSP²結合(二重結合)によって構成された炭素原子のシート⁸⁾で、優れた電気的、光学的、化学的、熱的、機械的特性を備えている⁹⁾。このような興味深い利点を併せ持つグラフェンは、電子工学、エネルギー関連システム、検出素子、その他多くの用途の新たな選択肢として検討され

as the higher number of torpedo cars out of cycle, an increased demand for steel heating up processes consuming energy, and more important, a lower final product yield. There are many factors disturbing high productivity operation and one of the most concerning ones is the inefficient drainage of metal and slag, which rises the liquid level and causes instability of blast pressure and burden descent¹⁾. Tap hole clay plays a role of utmost importance in this scenario, as the flow rate of slag and metal being drained out of the furnace is directly related to the degree of erosion of the tap hole area. Kitamura et al²⁾ and Youn et al³⁾ evaluated different tap hole clay formulations, pointing out the best combinations for improved corrosion resistance which could, as a consequence, lead to a stable pig iron production.

That means that besides guaranteeing a suitable flow of liquids, the tap hole clay bears also the task of building and keeping a long and robust mushroom in order to better protect the inner walls around the tap hole⁴⁾. Tsuchiya et al⁵⁾ conducted a post-mortem analysis of a blast-furnace after the ending of its campaign and concluded that the tap hole length may change depending on the deadman position, which could consequently affect the mushroom stability.

On the top of that, recent cost-reduction practices applied in blast-furnace operations have significantly affected the standard in-furnace conditions, switching towards a circumferential metal flow and a more aggressive slag chemistry^{4),6)}. Regular tap hole clays available in the market have been struggling to perform well in such an unfavorable condition, mainly because no breakthrough technology has come up in terms of clay formulation in the past twenty years.

Standing out from this stagnation process, Sako et al developed in 2017⁷⁾ a novel technology based on a suitable plastic behavior and strong adhesiveness, by combining an optimized grain size distribution and an extremely efficient defloculant additive. The main target behind that idea was to supply a tap hole clay which was able, firstly, to fill in properly all the tap hole, without any molten metal infiltration or sealing

ている¹⁰⁾。グラフェンを活性化状態にするには大きな活性化エネルギーが必要で、反応を開始させるためには高い活性能力を有する物質が必要である。このグラフェン構造は耐火性が極めて高く、スラグやメタルによる侵食は極僅かであるため、マッド材の新材質として最適である。

本研究では、新規炭素含有特殊添加物 (CCSA) を最新のマッド材配合に添加することにより加熱中にグラフェン状構造が形成され、高い機械的強度と優れた溶損挙動を示し、実炉において堆積基盤の形成による出銑孔深度の伸長かつ安定化が認められたことについて報告する。

2. 開発

2.1 供試試料と実験方法

2.1.1 配合

マッド材中のグラフェン状構造の形成および利点を評価するために、3水準の配合を準備した。それらは全て同じ化学組成で、添加剤の含有量のみが異なる (Table 1)。標準的な配合に対し、新規の炭素含有特殊添加物 (CCSA) を添加した配合で、CCSA添加量は0 %, 0.5 %および1.0 %とし、以降はStandard THM, CCSA THM AおよびCCSA THM Bと表記する。

2.1.2 熱力学的シミュレーション

炭素含有特殊添加物の有無によって、加熱下で生成する鉱物相をシミュレーションするためにFactSageソフトを使用した。生成相の計算は、Equilibモジュールを用い、データベースにFToxidおよびFact53を選択して、200 °C、600 °C、1000 °Cおよび1400 °C還元雰囲気にて実行した。

problems, and then to stick firmly to the hearth wall and to the existing mushroom. Nonetheless, although that was indeed a powerful tool for the hearth walls protection, there was still room for corrosion resistance improvements in order to reach a stable metal production flow.

However, the main common added raw-materials are coke, pitch, tar or carbon black, which are comprised only by amorphous phases and do not tend to graphitize very easily. In other words, they fail in achieving a tough and non-wetting microstructure, which explains the above-mentioned ordinary performance of nowadays tap hole clay.

Thus, in order to complement the state-of-the-art hearth walls protection concept and reach the ultimate tap hole clay technology, this work presents an innovative solution for corrosion resistance based on the development of a graphene-like structure. Graphene is worldwide famous for being the first two-dimensional atomic crystal available, comprised of a sheet of sp^2 -hybridized carbon⁸⁾ and which provides excellent electrical, optical, chemical, thermal and mechanical properties⁹⁾. Due to such attractive compilation of advantages, graphene has been explored as alternatives for electronics, energy-related systems, sensors and many other applications¹⁰⁾. Therefore, chemical reactions of graphene have a large energy barrier, requiring highly reactive species to initiate the reaction, which makes this structure a perfect alternative for tap hole clay, as its refractoriness is extremely high and it could practically not be corroded by neither slag nor molten metal.

In the present work, by adding a new carbon-containing special additive (CCSA) into a state-of-the-art tap hole clay formulation, a graphene-like structure was developed during heating, providing very high mechanical strength (due to very strong carbon bonding) and excellent corrosion behavior, and guaranteeing an ultimate solution for a long lasting protective mushroom.

Table 1 Compositions of the evaluated tap hole clays, with different additives contents

Raw Materials	Standard THM	CCSA THM A	CCSA THM B
Al ₂ O ₃	20	20	20
SiC	21	21	21
Fe-Si ₃ N ₄	22	22	22
SiO ₂ +Si	19	19	19
CCSA	0	0.5	1
Others	8	7.5	7

2. 1. 3 X線回折(XRD)と走査型電子顕微鏡(SEM)

ラボ試験においてグラフェン状構造の形成が可能かを解析するため、X線回折およびEDS(エネルギー分散分光法)スポット分析を用いた走査型電子顕微鏡を用いた。Standard THMおよびCCSA THM Bを1450℃で焼成、粉碎後に325メッシュの篩に通し、X線回折分析を行った。また、1450℃で焼成した炭素含有特殊添加物を含むマッド材CCSA THM Bを研磨し、SEM-EDS分析用に金で被覆した。得られた結果は、熱力学シミュレーションと比較した。

2. 1. 4 機械特性

密閉混練方法に則って混練し、一軸圧縮成形して160 mm×40 mm×40 mmの角柱試料を得た。成型後の試料は還元雰囲気で800℃、1200℃および1400℃で焼成し、冷却後に試験した。

冷間圧縮強さ試験は、万能材料試験機 KRATOS (型式: KE-30.000/E MP)にて実施した。

2. 1. 4. 1 熱間曲げ強さ(HMOR)

熱間曲げ強さ(HMOR)測定は、ASTM C583規格に従って、800℃、1200℃および1400℃において3点曲げ試験にて行った。試料を150 mm×25 mm×25 mmの角柱試料に圧縮成形し、それぞれの試験温度で予め焼成し、その後冷却を行い、続いて試験中に再加熱した。

2. 1. 4. 2 侵食試験

侵食試験は400℃で予備焼成した試料を用い、バーナーで加熱した回転炉で行った。各試料の侵食試験前後の試料の厚さを測定し、耐食性指数は標準試料Standard THMを100として算出した。スラグ侵食については70 %スラグと30 %銑鉄の混合物を用い、一方、銑鉄侵食については80 %銑鉄と20 %スラグの混合物を用いた。用いたスラグの化学組成をTable 2に示す。侵食試験は、約1550℃で2時間の試験条件で行い、スラグと銑鉄の組合せた侵食剤は1時間毎に交換した。

Table 2 Chemical composition of the blast-furnace slag used in the corrosion tests

SiO ₂ / %	CaO / %	Al ₂ O ₃ / %	Fe ₂ O ₃ / %	MgO / %	MnO / %	Binary Basicity
34	45.5	10.4	0.4	5.5	0.7	1.3

2. Development

2. 1 Materials and methods

2. 1. 1 Formulation

Three compositions were selected to evaluate the formation of the graphene-like structure in the tap hole clay and its benefits. All of them present the same chemical composition, differing only on the additives contents (Table 1). A standard formulation was used as the base reference and two new compositions were developed by adding the new carbon-containing special additive (CCSA), in two different concentrations: 0,5 % and 1 %, hereafter denoted as "THM A and THM B", respectively.

2. 1. 2 Thermodynamic simulation

The FactSage software was selected to simulate the phase evolution during heating of the tap hole mix with and without the new carbon containing special additive. The calculations of the phases evolution took place at different temperatures: 200 °C, 600 °C, 1000 °C and 1400 °C at reducing atmosphere, using Equilib module. FToxid and Fact53 databases were selected for the calculations.

2. 1. 3 X-Ray diffraction (XRD) and scanning electron microscopy (SEM)

To analyze if the graphene-like structure could be formed in actual laboratory conditions, under the influence of reactions kinetic, X-ray diffraction and Scanning Electron Microscopy using EDS (energy dispersive spectroscopy) spotting analysis were conducted. Samples of Standard THM and CCSA THM B were fired, had ground and sieved through the 325 mesh sieve for the X-ray diffraction analyses. The Standard THM sample was fired at 1450 °C to be used as comparative figure of the existing phases, whereas for the CCSA THM B, and 1450 °C in order to analyze the presence of graphene-like structure. Besides that, one sample of THM with the carbon containing special additive fired at 1450 °C was polished and covered with gold to be analyzed using SEM technique and EDS. The attained results were compared with thermodynamic simulations to better understand the presence of graphene-like structure and its correlation with the results in

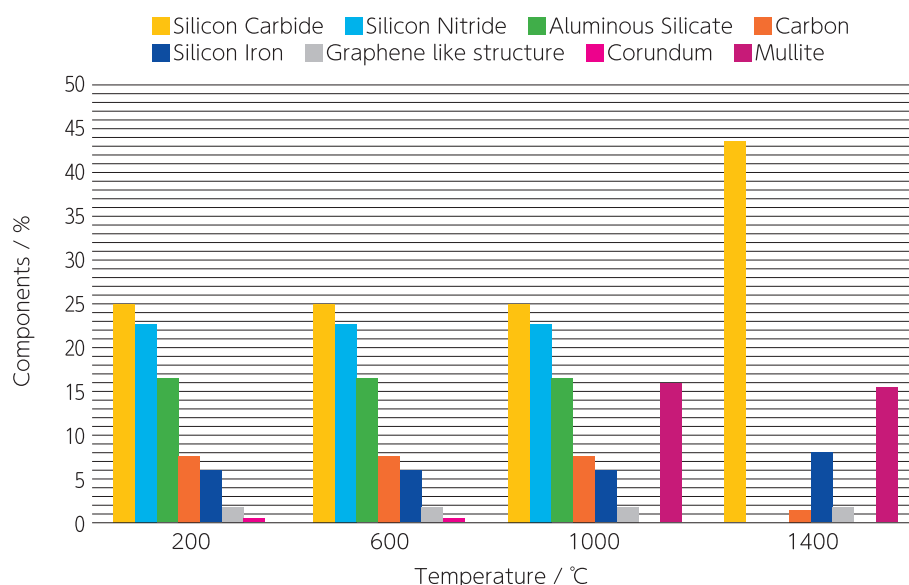


Fig. 1 Thermodynamic simulation results for CCSA THM B, pointing out the phases formed at 200 °C, 600 °C, 1000 °C and 1400 °C.

2. 1. 5 実炉試験

実炉において炭素含有特殊添加物を適用したマッド材の改善性能を評価するために、2基の高炉(本稿ではBF#AおよびBと表記)にて小規模試験を実施した。

1日の銑鉄生産量は、高炉Aで約7000 t、高炉Bで約8500 tである。

2. 2 結果と考察

Fig.1は、熱力学シミュレーションによってCCSA THM Bを各温度で還元焼成した際に生成する鉱物相の生成割合を算出した結果を示している。この結果から、非常に低い温度においてもCCSA THM Bにおけるグラフェン状構造

laboratory evaluation.

2. 1. 4 Physical properties

Prismatic samples (160 mm × 40 mm × 40 mm) were obtained by performing the mixing step according to an internal mixing procedure, followed by uniaxial pressing. After pressing, the samples were fired at 800 °C, 1200 °C or 1400 °C at reducing atmosphere, cooled down and tested.

The cold compressive strength test was conducted at Universal Testing Machine KRATOS (model: KE-30.000/E MP).

2. 1. 4. 1 Hot modulus of rupture (HMOR)

The Hot Modulus of Rupture (HMOR) measurements were carried out according to the ASTM C583 standard under three-point bending tests at 800 °C, 1200 °C and 1400 °C. The samples were pressed in a prismatic format (150 mm × 25 mm × 25 mm), pre-fired at their respective test temperature, cooled down, and then reheated during the test.

2. 1. 4. 2 Corrosion tests

The corrosion tests were conducted in a rotary furnace heated by torch on samples pre-fired at 400 °C. The samples' thickness was measured before and after the attack to provide the corrosion resistance index of each formulation. For the slag attack, a 70 % slag / 30 % pig iron mix was used,

Table 3 Description of phases presented at XRD analysis for Standard THM and CCSA THM B samples fired at 1450 °C

Formed Phases	Standard THM	CCSA THM B
Silicon Nitride	Present	Present
Aluminium Oxide	Present	Present
Silicon Carbide	Present	Present
Mullite	Present	Present
Graphite	Present	Present
Silica	Present	Present
Iron	Present	Not present
Graphene-like Structure	Not present	Present

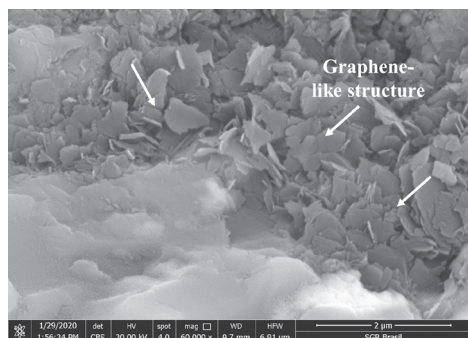


Fig. 2 Scanning Electron Microscopy (SEM) image showing the lamellar structure of the graphene-like phase obtained at CCSA THM B fired at 1450 °C.

の形成が可能なことは明らかであり、その構造は熱力学的に安定して系内に存在することが示唆された。

600 °C以下の低温域では、炭化珪素、窒化珪素、ケイ酸アルミニウム、炭素、金属シリコンおよびコランダムが観察される。1000 °Cでは、ケイ酸アルミニウムとコランダム相はもはや存在せず、ムライトが生成する。また、1400 °Cでは炭化珪素は増加し、炭素と窒化珪素は減少が認められる。ただし、グラフェン状構造は全温度域で安定して存在していることと、このシミュレーションは相の核形成と成長に対する活性化エネルギーのみを考慮した結果であることには注意を払う必要がある。むしろ、本来の使用状況下での相生成を鑑みると、活性化エネルギーおよび律速段階の両方を考慮しなければならない。

X線回折でグラフェン状構造を観測したように、試料を処理し1450 °Cで焼成して走査型電子顕微鏡 (SEM) で分析した。Fig.2に示すように、グラフェン特有のラメラ構造が、炭素含有特殊添加物を含有したマッド材CCSA THM Bで観察された。これは、XRDでグラフェン状の鉱物相の形成を証明しただけでなく、その相が優れた化学的、熱的、機械的特性を有する独自の2次元構造を形成したことも証明した。次項では、その特性が高炉操業をより安定化できることを立証するために、ラボと実炉での特性の比較解析を記載する。

Fig.3に、各試料の冷間圧縮強さを示す。炭素含有特殊添加物を含有したCCSA THM AおよびCCSA THM BはStandard THMと比較し、全温度における冷間圧縮強さの向上が認められる。

CCSA THM AおよびCCSA THM Bの3水準の温度にお

whereas for the pig iron attack, the mix comprised 80 % pig iron and 20 % slag. The slag chemical composition is presented at Table 2. The corrosion tests took place in two hours at a temperature around 1550 °C with the slag and pig iron combination changed each hour.

2. 1. 5 Field tests

After the lab tests, a pilot trial was conducted in two Brazilian blast furnaces (denoted here as BF#A and BF#B), aiming to validate the better performance of the carbon-containing special additive tap hole mix at field conditions.

The blast-furnace #A produces roughly 7000 t, and #B produces roughly 8500 t of pig iron per day.

2. 2 Results and discussion

Figure 1 shows the thermodynamic simulation for CCSA THM B at reducing atmosphere and at different temperatures. The results indicated the likelihood of the graphene-like structure formation in the CCSA THM B formulation even at very low temperatures, pointing out that such structure is thermodynamically stable and, therefore, its presence in the system is very favorable.

Initially, silicon carbide, silicon nitride, aluminous silicate, carbon, silicon and corundum are observed. At 1000 °C, aluminous silicate and corundum phases are not present anymore, giving rise to the formation of mullite. Finally, at 1400 °C, an increase on the amount of silicon carbide and a decrease on the amount of carbon and silicon nitride is observed. It is important to note that the graphene-like structure remains stable at the whole temperature range and that the simulations only considered the thermodynamic barrier for nucleation and growth of a phase. However, when bearing in mind the in situ formation of phases, both the thermodynamic and kinetic barriers must be considered.

As seen the presence of graphene-like structure at X-ray, the sample was treated and fired at 1450 °C and analyzed at Scanning Electron Microscopy (SEM). A lamellar structure typical of the graphene was identified in the tap hole mix with carbon-containing special additive, as described in Figure 2. This is a very relevant result, as it proves that not

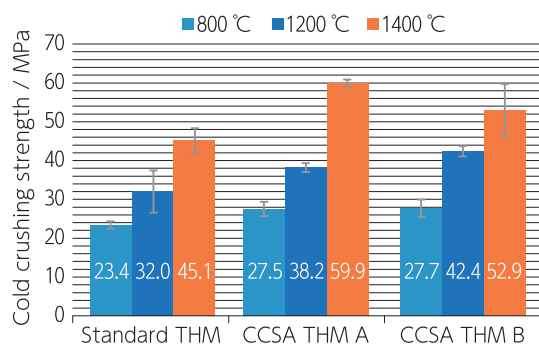


Fig. 3 Cold crushing strength of the evaluated materials after heat-treatment at 800 °C, 1200 °C and 1400 °C.

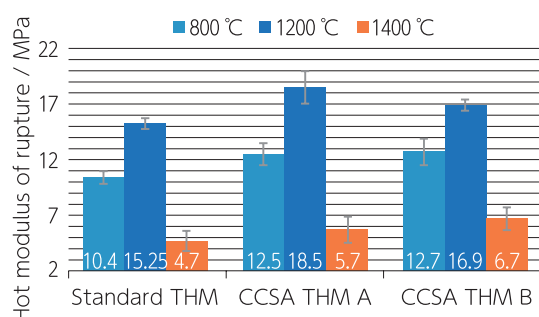


Fig. 4 Hot modulus of rupture values for “Standard THM”, “CCSA THM A” and “CCSA THM B” samples attained at 800 °C, 1200 °C and 1400 °C.

ける機械的抵抗の上昇には、冷却状態で高い機械強度を示しうるガラス相の形成が影響した可能性がある。耐火物原料に内在する液相形成に寄与する可能性がある不純物を加味していない点で熱力学的シミュレーションは不完全であるため、異なる温度(800 °C, 1200 °C, 1400 °C)で3つの試料の熱間曲げ強さを測定した。Fig.4の結果から、機械的挙動の改善はグラフェン状構造の存在に起因するものであり、液相とは無関係である。炭素含有特殊添加物を含む試料CCSA THM AおよびCCSA THM Bは全温度域で熱間曲げ強さが増大し、1400 °CではCCSA THM Bの熱間曲げ強さが最も高かった。

グラフェン状構造が濡れ難い特性をもつだけでなく、高温での機械的挙動を改善することは、耐食性を向上させる上でより有利である。Fig.5は、Standard THMを100として各試料のスラグおよび銑鉄侵食試験後の損耗量を指数化して表わしたものである。グラフェン状構造は銑鉄およびスラグとの反応性が低く、効果的であったことが明白であり、スラグおよび銑鉄の両方との相互作用を減少させ、

only was the graphene-like phase formed, as already verified via the XRD technique, but that the phase was surely generated in the unique 2D-structure which guarantees excellent chemical, thermal and mechanical properties. Comparative analyzes of properties at laboratory and field scales will be presented in the next section in order to confirm the better performance which could promote a stable blast furnace operation in the steel industry.

Analyzing the results of cold crushing strength of Standard THM, CCSA THM A and CCSA THM B in Figure 3, it is possible to observe an improvement in the cold crush strength in all temperatures of the formulations containing the special additive.

As CCSA THM A and CCSA THM B samples showed an increase in mechanical resistance at the three evaluated temperatures, there was a suspicion of the formation of glassy phase which could lead to higher cold mechanical strength. As the thermodynamic simulation was not enough, because it did not consider the impurities that are inherent in refractory raw materials and could result in the formation of liquid phases, hot modulus of rupture was measured for the three samples at different temperatures (800 °C, 1200 °C and 1400 °C). From the results present in Figure 4, the better mechanical behavior is due to the presence of the graphene-like phase, with no relation to any liquid phase. The CCSA-containing samples showed the highest values of HMOR at the whole temperature range, with CCSA THM B showing the best result of hot mechanical resistance at 1400 °C.

The better hot mechanical behavior, as well as the low wettability features of the graphene-like structure, more favorable are the aspects for achieving an increased corrosion resistance. Figure 5 presents the wear resistance after slag and pig iron attack in a rotary furnace for the three evaluated compositions, using the Standard THM sample as the main reference. It is straightforward to notice the benefits of the low reactivity of the graphene-like phase, reducing the interaction with both slag and pig iron and, consequently, decreasing the wear of CCSA THM A and CCSA THM B samples. In fact,

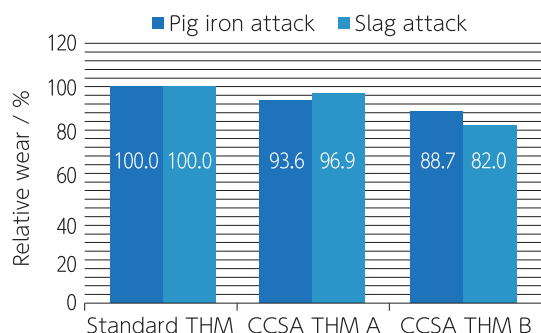


Fig. 5 Wear resistance after slag and pig iron attack for the three evaluated compositions. The results are expressed in a relative index, considering the Standard THM as the reference.

CCSA THM AおよびCCSA THM Bの損耗量を減少させたと考えられる。実際CCSA THM Bは、優れた耐食性を示し、スラグ侵食に対しておよそ20%の低減を示し、これは配合中の炭素含有特殊添加物の含有量が多いことが影響していると考ええる。

ラボ試験での良好な結果を受け、この新開発した高性能マッド材を実炉試験した。高炉Aでは、メンテナンスによる停止が近く、深度を伸ばすことが必要なことから、この新開発した高性能マッド材を出鉄孔#1に適用した。

Fig.6に、高炉Aにおける通常のマッド材と新開発した高性能マッド材の出鉄孔深度を示す。新開発した高性能マッド材は、出鉄孔深度の伸長と維持能力が明確に認められ、このマッシュルームの安定性から炉内および出鉄孔周辺が良好に保護されていることが分かる。

CCSA THM B showed an outstanding performance, with roughly 20 % reduction on the slag corrosion, which is directly related to the higher content of the carbon containing special additive present in its formulation.

The clay followed to field tests after the good results at laboratory tests. At blast furnace “A”, this type of clay with special properties were mainly used at tap hole #1 due its difficulties to achieve higher lengths because of an advanced campaign, closer to maintenance stoppage.

The ability of increasing and maintaining the tap hole length was clearly observed when comparing the results of the regular clay to the new developed high performance tap hole clay, as showed in Figure 6. The mushroom stability shows that the area inside the furnace and around the tap hole is well protected.

Analyzing the use at blast furnace “B”, where Shinagawa has a higher participation in use of tap hole clay, once can see the stability of tap hole length over the days in a large period of use as shown in Figure 7.

Additional to the tap hole length stability, a tendency of coke rate decreasing is presented in Figure 8. As coke is the main fuel of blast furnace, the result is related to less carbon loaded at the furnace.

This relation is not easy and simple to make, the conditions of operation of furnace was quite

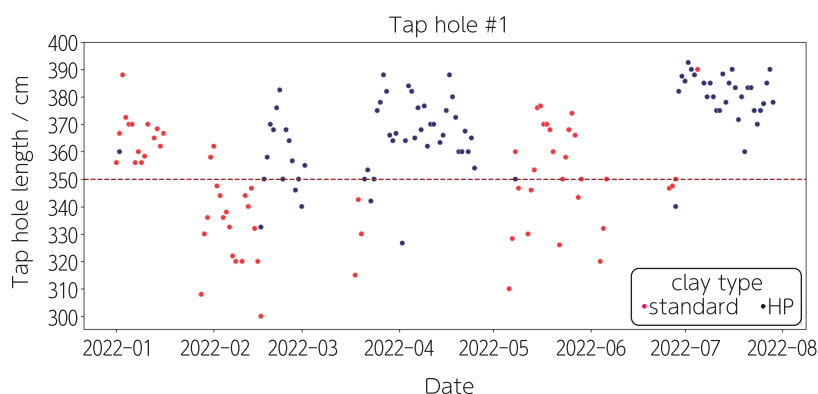


Fig. 6 Tap hole length comparing Shinagawa High Performance Clay with regular clay over days at blast furnace “A”.

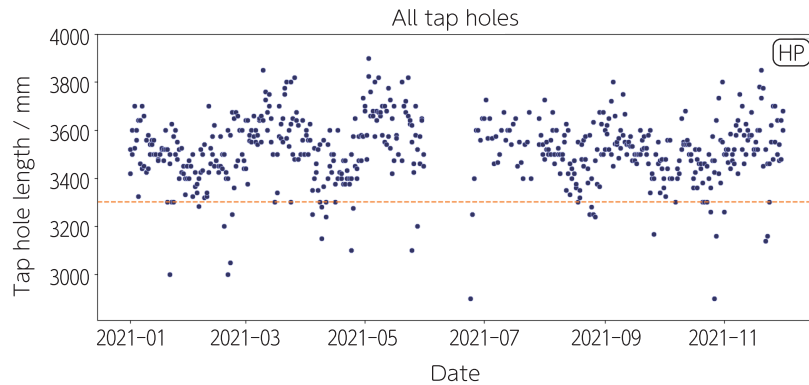


Fig. 7 Tap hole length with Shinagawa High Performance Clay over days at blast furnace “B”.

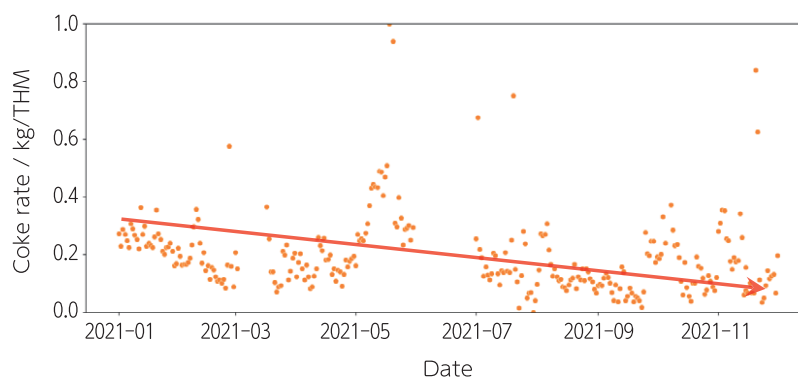


Fig. 8 Coke rate at blast furnace “B” over days.

品川リフラクトリーズ ブラジル製マッド材の使用割合が高い高炉Bでの新開発の高性能マッド材の使用状況をFig.7に示す。長期に渡って出銑孔深度の安定性が確認できる。

Fig.8に、高炉Bにおけるコークス比率を示す。コークス比率は減少傾向を示しており、コークスが高炉の主燃料であることから、高炉への炭素装入量が低下傾向にあったと考える。

コークス比率の低下は容易かつ単純に起こることではなく、世界的な経済情勢の影響により炉の操業条件は過去数ヶ月間、極めて複雑だった。言い換えれば、高炉の安全で持続可能な操業をする上で、新開発した高性能マッド材が良好に作用することを示唆している。

3. 結論

本研究では、炭素含有特殊添加物の添加によってグラフェン状構造を有し、優れた化学的、熱的、および機械的特性を示すマッド材技術を紹介した。熱力学的シミュレー

complicated last months due global economic condition. Even though, the results have indicated a positive effect of an engineered and high-performance refractory on a safe and sustainable operation of blast-furnaces.

3. Conclusion

An ultimate tap hole clay technology was presented in this work, based on the introduction of a graphene-like structure by adding a carbon containing special additive, which was able to provide excellent chemical, thermal and mechanical properties. Thermodynamic calculations and microstructural analyzes showed the stability of such phase in the tap hole clay structure, whereas laboratory tests confirmed its main benefits: higher mechanical strength and enhanced corrosion resistance.

The field tests in two different blast-furnaces with large production pointed out that the excellent

ションと微構造組織観察ではマッド材組織でのそのような相の安定性を示した一方で、冷間圧縮強さや熱間曲げ強さといった機械的強度の向上と耐食性の強化を確認した。

生産量の多い2基の高炉における実機試験では、ラボ試験で確認された優れた特性が、安定した出銑孔深度で操業させ、安定出銑と炉壁保護に影響していることが示唆された。炉壁保護の改善も観察できており、結果としてマッド材消費量が低減し、マッド材生産原料が削減され、炉に装入される燃料が低減し、言い換えれば、炭素使用量が削減される可能性がある。

何れの結果も、この新技術がもたらした画期的な進歩を証明するものであり、また操業条件が絶えず変化する現状においても高い性能を維持できていた。

properties of the novel tap hole clay observed in the laboratory were responsible for making the furnace operate with stable tap hole length which is related with stable drainability and hearth protection. A better protection of the hearth walls could also be observed, consequently reduce consumption of clay, less use of raw materials to produce clay and possibility of decreasing use of fuel loaded at furnace, in other words less carbon used.

Both results evidenced the breakthrough advance brought by this novel technology, which was able to keep high performance even during the current scenario of constant changing of operational conditions.

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