

転炉補修用吹付材の開発

Development of Carbon Bonded Gunning Mix for BOF

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Abstract

We studied some different softening point pitches as binders for Carbon bonded gunning materials and additive amount of another molar weight phenolic resin.

As a result we found a good composition which gives high adhesion strength, high adhesion rate and hardening time.

Based on the result. We used the developed item in a BOF and confirmed high adhesion ability and good durability.

1. 緒 言

転炉の熱間補修では、主に吹付補修材と焼付補修材が使用されている（Fig. 1）。吹付補修材は、焼付補修材で補修できない部位に使用され、磷酸ボンド吹付材とカーボンボンド吹付材が各々の特徴を活かし（Table 1, Fig. 2）の部位に使用され効果を上げている。特にトラニオン側や高温のスラグ侵食を受けるスラグライン、出鋼口周辺については、磷酸ボンド吹付材と比較し耐溶損性・耐剥離性に富んだカーボンボンド吹付材が広く使用されている。そこで、さらなる高耐用化・高接着性を目標とし高カーボンボンド吹付材の改良を行った。

2. カーボンボンド吹付材の特徴と開発の考え方

カーボンボンド吹付材は、粒度調整されたマグネシア骨材とカーボンバインダーにて構成されている。このため、低融物の生成が少なく、カーボ

1. Introduction

Gunning repair mixes and hot casting mixes are the main materials for BOF hot repair (Fig.1). Hot gunning repair, phosphate bonded structures and carbon bonded structures, are used mainly for areas that can't be repaired with hot casting mixes (Table 1, Fig.2). Especially, The carbon bonded gunning mixes are generally applied to the trunnion sides, the slag attacked areas and area surrounding the tap hole. So carbon bonded gunning mixes of high durability and high adhesion have been developed.

2. Characteristics and Concept of Carbon Bonded Gunning Mixes

Carbon bonded gunning mixes consist of magnesia raw materials with adjusted grain

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Fig. 1 Gunning on inner wall of BOF in hot condition.

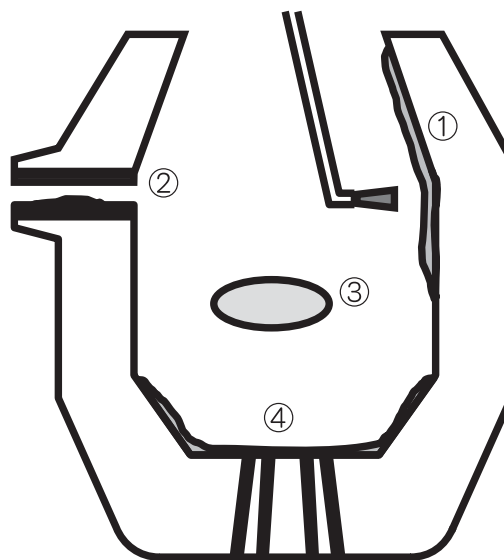


Fig. 2 Diagram of repaired area.

Table 1 Repaired area of BOF

Repaired part	Required properties	Material
①Cone	Protection of wall	Phosphate bonded gunning mixes
②Tap hole area	Quick hardening High Durability	Hot casting repair mixes (Water binder system or Carbon binder system)
③Trunion sides	High Durability High adhesive strength	Carbon bonded gunning mixes Phosphate bonded gunning mixes
④Charging side wall	Quick hardening High Durability	Hot casting repair mixes (Carbon binder system)

ンによって過焼結とスラグ浸潤を抑制しており、その結果、使用中の剥離脱落が少なくなり、高い耐用性を示す。以下に従来からの燐酸ボンド吹付材と比較したカーボンボンド吹付材の特徴を示す。

- ①高温における接着強度が高い。
- ②収縮の程度が小さく、剥離損傷が少ない。
- ③スラグの浸潤が少なく、耐食性が高い。
- ④燐酸塩を含まない。
- ⑤従来の乾式吹付材と同じ吹付装置が使用できる。

水と混合された吹付材は塑性流動を示し、炉壁に吹き付けられた時、流れ落ちずにその場に止まる。次に水分が蒸発し、バインダーの融解・ゲル化が起こる。最後にカーボンボンドが形成され、壁面と強固に接着する。従って、カーボンバインダーはカーボンボンド吹付材の最重要ポイントであると考ええる。

size and carbon binder. Carbon bonded gunning mixes contain less low melting point components. Consequently carbon bonding restrains over-sintering and slag penetration. As a result, carbon bonded gunning mixes have the qualities of low peeling damage and high durability. The special features of our carbon bonded gunning mixes which are not found in conventional phosphate bonded gunning materials are as follows ;

- ①High adhesive strength in hot conditions.
- ②Peeling damage occurs little because of low shrinkage value.
- ③Low slag penetration and high corrosion resistance.
- ④Contain no phosphate.

Table 2 Properties of magnesia clinker

Chemical composition MgO (mass%)	95
Grain size distribution Max. size (mm)	3
>1.0mm (%)	28
<0.075mm (%)	38

Table 3 Properties of pitch powder

	Softening point	Fixed carbon (mass%)
A	High	80
B	Middle	70
C	Low	60

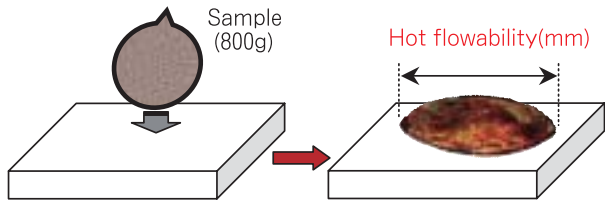


Fig. 4 Measurement of hot flowability.

今回、カーボンバインダーとして、ピッチ原料およびフェノール樹脂の種類と添加量に着目し、各種検討を行った。

3. ピッチの検討

3. 1 試料

試料は粒調したマグネシアクリンカーに軟化点の異なる3種類のピッチを外掛け $\alpha \sim 4\alpha$ %添加し調製した。Table 2 にマグネシア原料の特性を示す。Table 3 に検討したピッチの特性を示す。試料は厚さ0.02mmのポリ袋詰とし、800g 詰めたものを展開性測定用、150g 詰めたものを接着強度測定用として作製した。

3. 2 熱間展開性の測定

Fig. 3 に示す小型加熱炉を加熱し、十分に蓄熱させた後に熱間（1000℃）で試験を行った。キャストابل板の上にポリ袋入りの試料を乗せ、燃焼が終了するまで保持した。その後キャストابل板

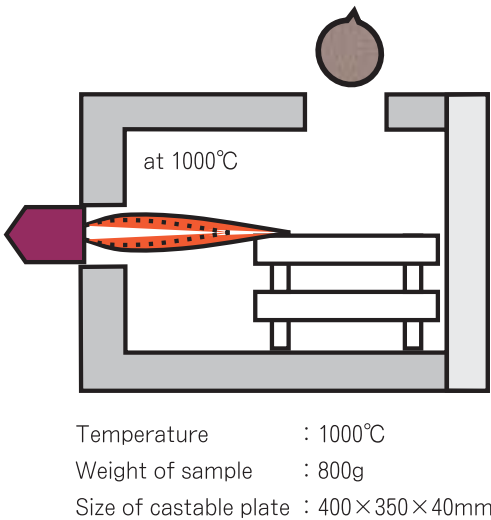


Fig. 3 Diagram of small examination furnace.

⑤Conventional gunning equipment can be used.

The wet gunning mix stays on the wall because it is in a plastic state. Next, water vaporization occurs, followed by the melting and gelation of binder, after which carbon bonding occurs causing the gunned mix to adhere strongly to the hot wall. Therefore the carbon binder is the most important for element of carbon bonded gunning mixes.

In this study, as a carbon binder we researched kinds and contents of pitches and phenolic resins.

3. Study of Pitch

3. 1 Sample

Samples were prepared with pitch of three types from $\alpha \sim 4\alpha$ added to the magnesia grains. Table 2 shows the characteristics of magnesia. Table 3 shows the characteristics of the pitch powders. 800g samples were used for measuring hot flowability and 150g samples were used for measuring hardening time and adhesion intensity.

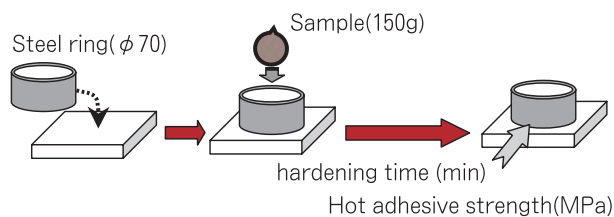


Fig. 5 Measurement of hardening time and adhesion intensity.

ごと取出し、試料の流動後の直径、厚さを測定した (Fig. 4)。

3. 3 接着強度の測定

Fig. 3 の炉内で1000℃に加熱したマグネシア質れんが (114×112×30mm) の上に内径φ70×40mmの鉄製リングを載せ、リング内に試料150gを投入し炎が消えるまでの時間を硬化時間として測定した (Fig. 5)。また、接着強度は消火後直ちにFig. 6 に示すせん断接着測定装置で測定した。

3. 4 試験結果

試験結果をFig. 7 に熱間展開性, Fig. 8 に接着強度, Fig. 9 に硬化時間を示す。軟化点の低いピッチほど熱間での高い流動性を有する (Fig. 7)。吹付材においては、吹付面から流れるようでは施工性に悪影響を及ぼすため高展開性のピッチは不向きである。また、接着強度は軟化点の低いものほど高い傾向となる (Fig. 8)。これは熱間での粘性の違いが接着界面へ影響しているものと考えられる。ピッチBについては熱間での流動性も低く、また接着強度も高いことから吹付材に適して

3. 2 Measurement of hot flowability

The hot flowability was measured in a small furnace at 1000℃ as shown in Fig.3.

The repair mixes were placed on a castable board in the furnace until the end of combustion. The diameter and thickness of each sample was measured after combustion. (Fig.4)

3. 3 Measurement of adhesion intensity

An iron ring was placed on a magnesia brick (114×112×30mm) and heated at 1000℃. 150g of the repair mix was supplied in a ring (φ70×40mm). The time in which the flame disappeared was the hardening time. (Fig.5) Adhesion intensity was measured with the equipment shown in Fig.6 after hardening.

3. 4 Examination results

Fig.7 shows the hot characteristics, and Fig.8 shows the adhesion intensity, and Fig.9 shows the hardening time.

The lower flexibility point pitch possess high flowability in hot conditions. (Fig.7)

A high flow ability pitch is unsuitable for gunning mix because if the gunning material doesn't remain on the gunned surface it has a bad influence on construction.

Lower softening point pitch shows higher adhesion intensity (Fig.8).

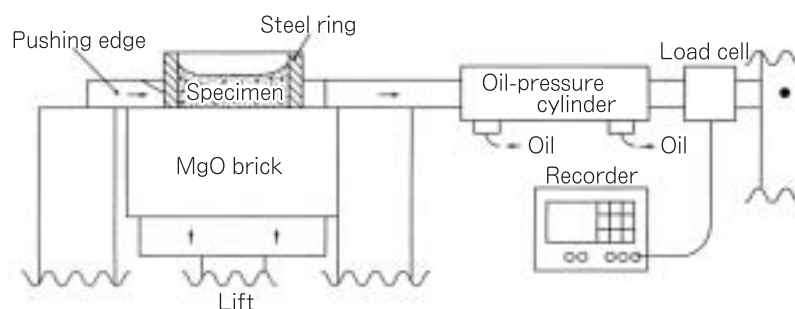


Fig. 6 Testing apparatus for adhesive strength.

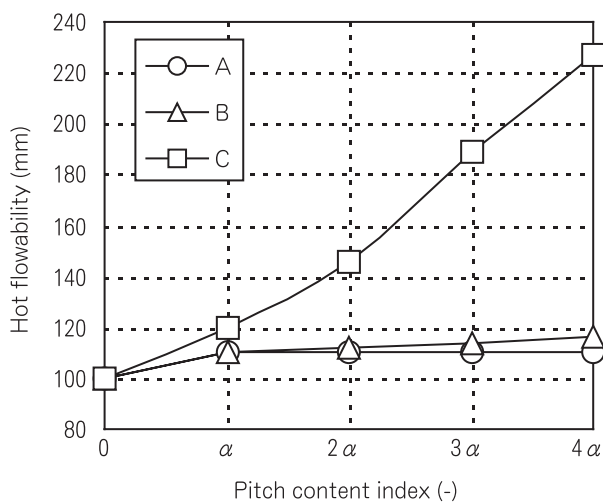


Fig. 7 Relation between pitch content and flowability at 1000°C.

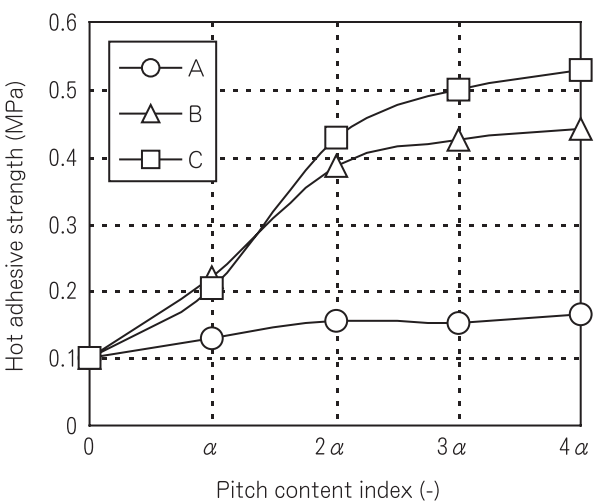


Fig. 8 Relation between pitch content and hot adhesive strength at 1000°C.

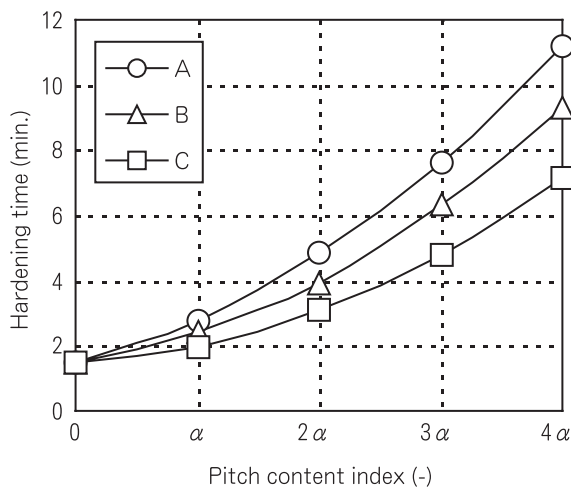


Fig. 9 Relation between pitch content and hardening time at 1000°C.

いると考えられる。また添加量は $2\alpha\%$ から接着強度の変化量が小さくなっていることと、硬化時間を考慮しピッチBを $2\alpha\%$ 添加と選定して以後の試験を行った。

4. フェノール樹脂の検討

4. 1 試料

フェノール樹脂が与える接着性について検討を行った。バインダーとしてフェノール樹脂を添加することにより、初期の接着強度が発現し接着性が向上すると考えられる。検討したフェノール樹

Table 4 Properties of phenolic resin

	Molecular weight
H	High
M	Middle
L	Low

This tendency shows that the difference in viscosity under hot conditions influences the boundary surface.

Pitch B is suitable for gunning materials because it shows low flow ability in hot conditions and high adhesion intensity.

$2\alpha\%$ of Pitch B was added to the test sample because the hardening time was short and the adhesion strength was high. It was examined thereafter.

4. Study of Phenolic Resin

4. 1 Sample

A relationship with phenolic resin was studied about adhesion intensity.

It was though that adhesion ability was advanced by adding phenolic resin. Phenolic resin with three different kinds of molar weights was studied. The characteristics are

Table 5 Mix composition of sample

Sample	No.1	No.2	No.3	No.4	No.5	No.6	No.7	No.8	No.9
Magnesia material	100	100	100	100	100	100	100	100	100
Pitch powder B	2 α	2 α	2 α	2 α	2 α	2 α	2 α	2 α	2 α
Phenolic resin H	β	2 β	3 β						
Phenolic resin M				β	2 β	3 β			
Phenolic resin L							β	2 β	3 β

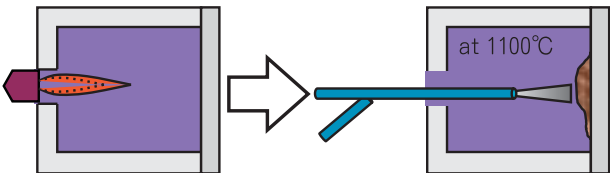


Fig.10 Diagram of large-sized examination furnace.



Fig.12 Gunning examination photograph.

脂は分子量の違うものを3種類選定した。その特性をTable 4に示す。Table 5に示すピッチB+フェノール樹脂で試料を調製した。

4. 2 吹付試験方法

Fig.10に示す大型吹付試験炉を十分に加熱し、1100℃の炉内で吹付試験を行った (Figs11, 12)。吹付装置の仕様および条件をTable 6に示す。吹付後パネルは台車により炉外へ移動させ、接着量を測定し接着率として算出した。

4. 3 試験結果

フェノール樹脂の種類および添加量と接着性の関係をFig.13に示す。いずれのフェノール樹脂も添加量と共に接着性が向上する結果となった。中



Fig.11 Gunning examination set up.

shown in Table 4. The sample was made with pitch B which is shown in Table 5 and phenolic resin.

4. 2 Gunning test method

The gunning test was examined at 1100℃ by using a big gunning test furnace which is shown Fig.10 (Fig.11, 12).

The specific of gunning equipment and conditions are shown in Table 6.

After the gunning test the panel was taken out of the furnace. We calculated the adhesion rate based on adhesion amounts.

4. 3 Experimental result

The kind of phenolic resin, additive amount and adhesion intensity are shown in Fig.13. Results show that adhesion intensities are proportionate to additive amount for any kind of phenolic resin.

Among them, phenolic resin M (middle amount of molar weight) had the best

Table 6 Condition for gunning

	Capacity	Air pressure	Hose length	Nozzle length
ROTEKTOR	0.2m ³	0.2MPa	10m	5m

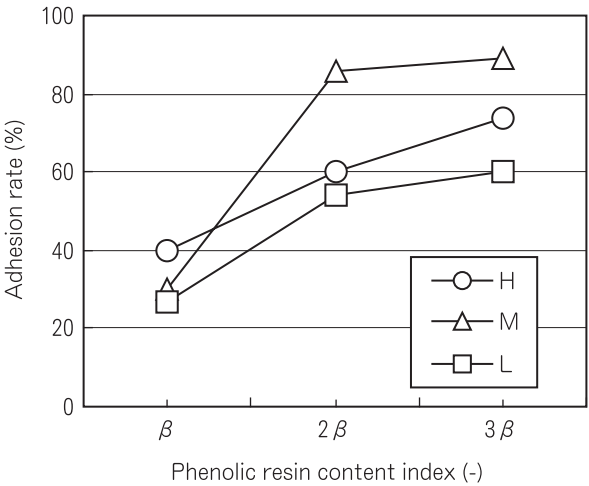


Fig.13 Relation between adhesion rate and phenolic resin content (type).

Table 8 Performance results for carbon bonded gunning mixes

Repaired area	Trunion sides		Slag line
Temperature (°C)	1000~1200	1000~1200	1000~1200
Mix consumption (kg/time)	500	1000	1000
Hardening time (min)	10	10	15
Durability (heats)	10	7	3~4

でもフェノール樹脂M（分子量の中程度のもの）が最も良好な結果であった。しかし、フェノール樹脂3種類ともに3β%まで添加すると収縮が大きく施工体に反りが発生する傾向が認められたため、接着率が最も良好であったフェノール樹脂Mの添加量は2β%が好ましいことが判明した。

5. 開発品の品質と実炉試験結果

試験結果から選択した試料5の品質をTable 7に示す。また今回開発したカーボンボンド吹付材の実炉適用実績をTable 8に示す。開発品の接着性は良好であり、また高耐用を示し転炉の寿命延長に貢献している。現在も各所にて実炉試験推進中である。

Table 7 Properties of carbon bonded gunning mix

	Newly developed mix
Chemical composition (mass%)	
MgO	78
C	9
Grain size distribution	
Max. size (mm)	3
>1.0mm (%)	28
<0.075mm (%)	38
Physical properties (after 1000°C)	
Apparent porosity (%)	31.5
Bulk density (-)	2.79

results.

But all of the three kinds of phenolic resins has a tendency for 3β% additive to cause large warpage to the gunned body. We studied the amounts of phenolic resin M addition which give the highest adhesion rates of better than 2β%.

5. Quality and Real Furnace Experimental Results

The quality of sample 5 which was selected from the experimental results is shown Table 7.

The results of application to carbon bonded gunning materials which we developed for BOF are shown in Table 8.

New products have good durability, high adhesion ability and render long BOF service life.

We still continue actual furnace experiments at various places.

6. まとめ

カーボンボンド吹付材におけるバインダーとして、軟化点の異なるピッチ、また分子量の異なるフェノール樹脂の添加量の検討を行った結果、接着強度、接着率、硬化時間において最も良好な組成を見出した。また、その結果を基にした開発品を実炉に適用し、高接着性でありかつ高耐用であることを確認した。これにより転炉の寿命延長に貢献しており、現在も接着性および耐用性の確認・調査を進めながら実炉試験推進中である。

6. Conclusion

We studied some different softening point pitches as binders for carbon bonded gunning materials and additive amount of another molar weight phenolic resin.

As a result we found a good composition which gives high adhesion strength, high adhesion rate and hardening time.

Based on the result. We used the developed item in a BOF and confirmed high adhesion ability and good durability.

It contributes to long BOF service life.

We continue actual furnace experiments on adhesion ability and durability.