

SHINAGAWA TECHNICAL REPORT

加熱炉スキッドパイプ用高耐用こて塗り補修材 “CCT-A620T”

High-Durability Troweling Repair Refractory
Material, CCT-A620T, for Reheating Furnace
Skid Pipe

塚 田 凌
Ryo TSUKADA

籠 貴 大
Takahiro KAGO

小 森 繁
Shigeru KOMORI



製品紹介／PRODUCT

加熱炉スキッドパイプ用高耐用こて塗り補修材 “CCT-A620T”

High-Durability Troweling Repair Refractory Material, CCT-A620T, for Reheating Furnace Skid Pipe

塚 田 凌^{*1}
Ryo TSUKADA籠 貴 大^{*2}
Takahiro KAGO小 森 繁^{*3}
Shigeru KOMORI

要 旨

膨潤性に優れた粘土を採用することで、コロイダルシリカを適用した高耐用こて塗り補修材を開発した。従来のセメント品と同様に施工でき、亀裂や剥離損傷の軽減による耐火物使用量の削減が可能である。

Abstract

By applying clay with a good swelling property, a high durability troweling repair refractory material, in which colloidal silica is used as binder, was newly developed. Similar to conventional cement blended troweling repair refractory, the newly developed troweling repair refractory, CCT-A620T, is applicable for repair work on reheating furnace skid pipe. Since damage caused by cracking and/or peeling-off is reduced through the use of CCT-A620T, the reduction of repair refractory consumption is achievable.

1. 緒言

加熱炉とは鑄造により得られた半製品である鋼片を加熱し圧延設備へ送り出す設備である。炉内耐火物は長期間高温で保持され、鋼片の表面酸化によって生じるスケールと反応するため、耐熱スポーリング性と耐FeO性が求められる。一方で、昨今のカーボンニュートラル達成の観点から、加熱炉から排出される熱を低減させることは極めて重要で、セラミックスファイバーの適用やCA₆キャストブルが使用される機会が増えている。しかしながら、セラミックスファイバーはFeOやミスト冷却による影響で耐用性が低下するなど、補修頻度の増加が課題である。そのため、依然として、使用する耐火物の高耐用化のニーズがあり、当社はスキッドパイプ用にコロイダルシリカを活用したケミカルボンドキャストブルを開発し¹⁾、長期間使用されても亀裂、剥離が少ないとの評価を受けている。一方で、従来のセメントキャストブルが施工されているスキッドパイプは、熱衝撃やFeOとの反応により激しく損傷する。定期

1. Introduction

The reheating furnace is a facility in which steel semi-products produced in a caster are heated up for the hot rolling mill. Since refractories relined in the reheating furnace are exposed to high temperatures for a long period of time, during which refractories react with mill scale generated by surface oxidation of semi-steel products, thermal spalling resistance and erosion resistance to FeO are required for reheating furnace refractories. Application of ceramic fiber or CA₆ castable refractory in reheating furnace has increased because of the importance of reducing exhaust heat from the reheating furnace in consideration of carbon neutrality realization. However, increase in repair work frequency becomes problem, because of deterioration of ceramic fiber durability caused by FeO attack or mist cooling applied during periodical maintenance work. For this reason, better durability of reheating furnace refractories is still required. The authors' company

^{*1} 技術研究所 第2研究部 第2研究室 Unshaped Refractories R&D Sec., Research Dept. No.2, Research Center

^{*2} 技術研究所 第2研究部 第2研究室 室長 Chief Manager, Unshaped Refractories R&D Sec., Research Dept. No.2, Research Center

^{*3} 赤穂工場 第1製造室 室長 Chief Manager, Production Sec. No.1, Ako Plant

的な炉内点検の際に、解体して流し込み施工を行うが、工程期間が確保できない場合は、こて塗り補修材で部分的に補修するため、こて塗り補修材の高耐用化が求められる。

本報告では、スキッドパイプの損傷部位を補修し、長期間の使用に対応できる高耐用こて塗り補修材を開発したので報告する。

2. 加熱炉スキッドパイプの損傷形態

加熱炉の操業は900℃程度の比較的低温領域から1300℃を超える高温領域まで幅広く、炉修時にはミスト冷却を実施して常温まで冷却するなど、温度変動が大きい。また炉内には鋼片の表面酸化によって生じるスケールと呼ばれるFeOなどの鉄酸化物が飛散しており、使用される耐火物にとっては過酷な環境である。このような環境で使用するスキッドパイプに使用されるキャストブルは、熱スポーリングによる亀裂損傷や鉄酸化物との化学反応による浸潤と剥離が発生し、さらに進行するとスキッド内部の水冷管が破損する (Fig.1)。そのため、定期的な炉内点検時の補修が重要である。

developed a chemical bond castable refractory for skid pipe utilizing colloidal silica¹⁾, which has been used with good results of a long service life without severe cracking or peel-off damages. Skid pipe, which is relined with a conventional cement castable refractory, is severely damaged by thermal shock and/or erosion by FeO derived from mill scale. Damaged skid pipe refractories are dismantled and repaired with new castable refractory during periodical maintenance. When maintenance time is too short to repair skid pipe by relining with new castable refractories, repair work is carried out with troweling repair material. For such occasions, a high durability troweling repair refractory is required.

This article will introduce the newly developed troweling repair refractory, CCT-A620T, which can have a long service life at the repaired position in the reheating furnace skid pipe.

2. Damage Patterns of Reheating Furnace Skid Pipe Refractory

The operation temperature of the reheating furnace is in the range from roughly 900℃ to over 1300℃.

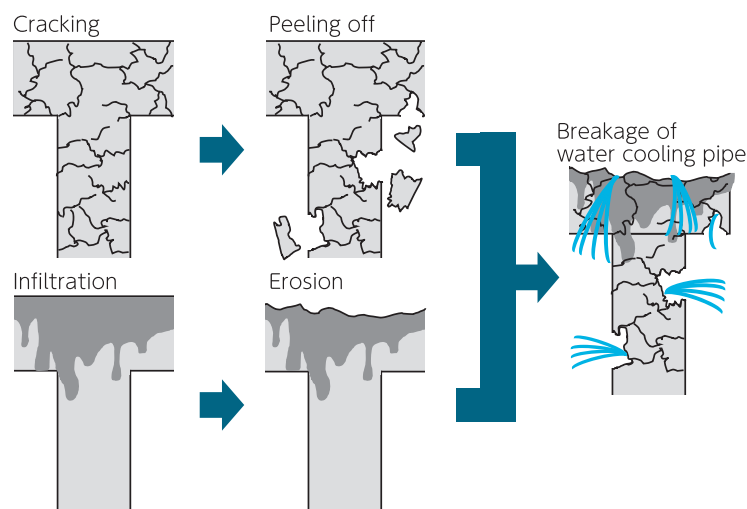


Fig. 1 Damage patterns of reheating furnace skid pipe refractory.

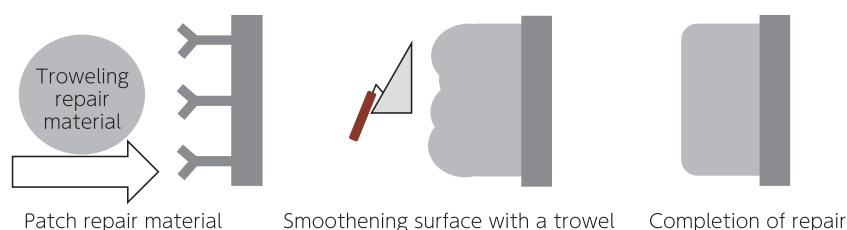


Fig. 2 Schematic diagram of troweling repair refractory application on skid pipe.

3. スキッドパイプ用こて塗り補修材の 施工方法

Fig.2に、スキッドパイプ用こて塗り補修材の施工方法の模式図を示す。施工方法はパッチング材に近く、硬めに混練した材料を手にとって施工部位に押し付け、施工体に水を塗布し、こてを用いて表面を均して施工する。この施工に対応するために、保形性、接着性、施工中の材料の湯き抑制の3つの特性が求められる。これらの特性を付与するため、適用する粘土種の選定が重要である。

4. 粘土の選定

粘土は天然に存在し、一般的に適度の水とよく混合した状態で可塑性が生じ、乾燥すると硬さを増し、焼成時に粘土の分解によって生じるシリカによる結合材の役割を果たす原料である。粘土原料は耐火物の微粉部に使用され、成形性向上や保形性の確保を目的として添加される。また、粘土の特性を評価する指標の一つとして膨潤性がある。膨潤性とは、粘土が水を吸収すると元の体積から膨らむ性質を意味し、膨潤性に優れるほど多くの水を吸収できると考えられる。

Fig.3に、粘土の膨潤性評価方法を示す。100mlの水を入れたメスシリンダーに2gの粘土を投入し、24時間後の容積を読み取り、膨潤性を数値化した。Table 1に試験に

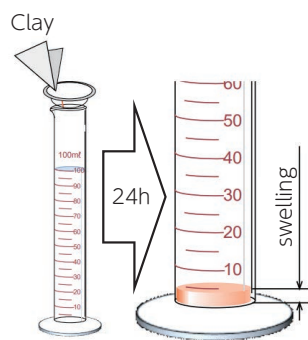


Fig. 3 Water dipping test to evaluate swelling property of clay.

Table 1 Chemical compositions of 3 kinds of clay

	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	Na ₂ O	K ₂ O
Clay A	64.1	17.6	5.7	1.0	0.8	1.2	2.7
Clay B	67.2	17.4	3.8	0.7	1.4	1.8	1.3
Clay C	70.4	15.5	2.0	1.6	2.4	2.3	0.3

Since relined refractories are cooled down by mist cooling during periodical maintenance work, they are exposed to large temperature fluctuations. In addition, reheated furnace refractories are exposed to a harsh environment where iron oxides, such as FeO, called mill scale is constantly being generated by surface oxidation of steel semi-products. As per Fig. 1, refractories relined on a skid pipe are damaged by cracks induced by thermal spalling, peeling-off caused by elongation of cracks, and/or infiltration of chemical compounds generated by reaction with iron oxides. When a refractory is severely damaged, the water-cooling pipe in the skid pipe is broken. Therefore, repair work on skid pipe refractories is necessitated during periodical inspections.

3. Relining of Troweling Repair Refractory on Skid Pipe

Fig. 2 is a schematic diagram of troweling repair refractory relining on a skid pipe. Firstly, troweling repair refractory kneaded to a relatively high hardness is patched on the skid pipe surface by hand. After patching, its water wet surface is smoothened with a trowel. Sufficient shape retaining property, good adhesiveness and adequate water holding property to suppress drying during relining work are required of troweling repair refractories. Thus, appropriate selection of the clay which is blended into the troweling repair material is important in order to secure these three characteristics.

4. Selection of Appropriate Clay

Clay, a common natural resource, generally exhibits a plastic property with a moderate amount of water addition as well as increased hardness as it dries. In the firing process, clay plays the role of binding blended raw materials through the silica components generated by decomposition. Clay is used as a fine raw material to secure moldability as well as shape retention of the green body. The swelling property is cited as one of the characteristics to evaluate clay material quality. Swelling is volume expansion behavior induced by water absorption. Clay with a good swelling property indicates that a large amount of water can be absorbed and held in the clay material.

The swelling property of three (3) kinds of clay was evaluated with the water dipping test shown in Fig. 3. In the example, two (2) grams of clay sample was dipped into 100 ml of water in a measuring cylinder. After keeping the clay in the water for 24 hours, the expanded volume of dipped clay sample

Table 2 Degree of swelling of each clay sample

	Clay A	Clay B	Clay C
	3.8	9.2	17.5
Swelling [ml/2g]			

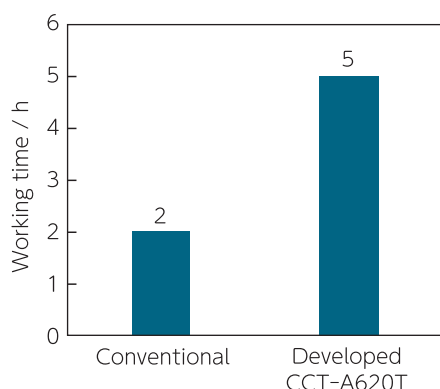


Fig. 5 Comparison of working time.

供した粘土の化学組成, Table 2に膨潤性を示す。粘土Cが明らかに優れた膨潤性を有する結果を得た。

Fig. 4に、粘土結晶構造と膨潤の模式図を示す。粘土は厚みが約1 nmの薄い板状結晶が積み重なった層状構造で、結晶層間にマイナスの電荷を帯び、陽イオンが吸着されている。層間に吸着している陽イオンは Na^+ , K^+ , Ca^{2+} , Mg^{2+} の4種類からなり、 Na^+ イオンを多く含むものをNa型と呼んでいる。膨潤は、模式図に示すように結晶層間に水分子が入ることで起こり、Na型が水中での膨潤、増粘、分散性が優れるとされており、今回の膨潤性評価結果とも合致する。

5. 開発品CCT-A620Tの特徴

5. 1 可使時間

コロイダルシリカを活用した材料の課題の一つに、材料表面の乾きがある。可使時間の確保が難しく、試作段階では2時間程度が限度であった。前述した膨潤性に優れた粘土を適用することで、材料の保形性を維持しながら添加水分量を増量させることができ、表面の乾きの抑制を実現した。その結果、開発品CCT-A620Tは可使時間を試作時の2倍以上である5時間まで延長 (Fig.5) し、実機の施工条件下でも施工可能な作業性を得ることができた。

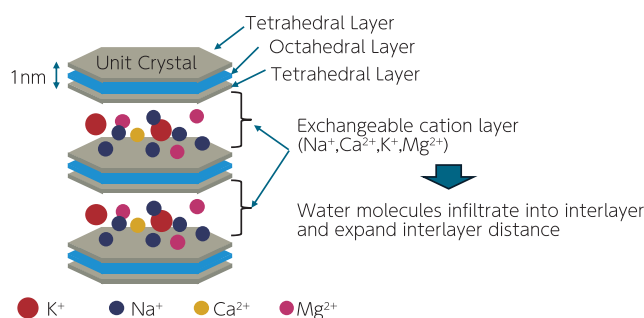


Fig. 4 Schematic illustration of crystal structure of clay mineral and mechanism of swelling.

was measured to quantify swelling behavior. The chemical compositions of three (3) kinds of clay are shown in Table 1. As per Table 2 in which the degree of swelling of each clay is compared, clay sample C exhibits the highest degree of swelling.

Fig. 4 schematically shows the crystal structure of clay and mechanism of swelling. Clay is composed of laminated plate crystal layers of approximately 1 nm thickness. Since the interlayer between plate crystals is charged with negative polarity, a variety of exchangeable cations, namely, Na^+ , K^+ , Ca^{2+} and Mg^{2+} , are absorbed. Clay largely containing Na^+ ion crystal interlayers is called Na-type clay. When water molecules infiltrate into the interlayer of clay, as illustrated in Fig. 4, the interlayer between the clay unit crystals expands, resulting in volume expansion, otherwise referred to as swelling. It is acknowledged that Na-type clay mineral exhibits a better swelling property associated with a high thickening property (increased viscosity) and good dispersibility in water. The results evaluated with the water dipping test are consistent with such knowledge.

5. Features of Newly Developed Troweling Repair Material, CCT-A620T

5. 1 Working life

One problem caused by the use of colloidal silica is quick drying of the refractory body surface. For this reason, the working time for troweling the refractory at the experimental stage was only 2 hours. When clay with a good swelling property was blended, the water component held in the refractory body notably increased, resulting in suppression of quick drying of the refractory body surface along with improved shape retaining property. As shown in Fig. 5, newly developed troweling repair material, CCT-A620T, realized a 5 hour working life, over two times that of its prototype product. In practical repair operations,

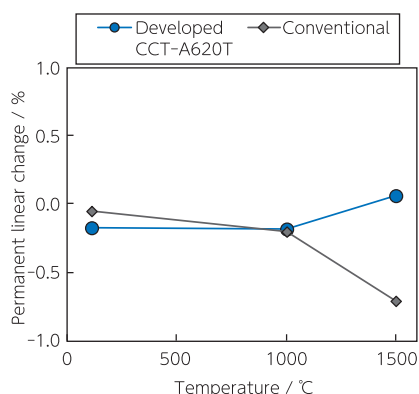


Fig. 6 Comparison of permanent linear change.

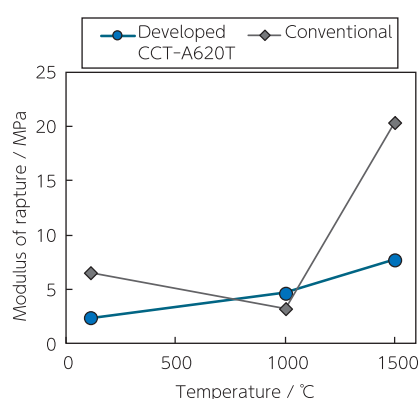


Fig. 7 Comparison of modulus of rupture.

5. 2 一般品質

セメントを使用した従来品にて塗り材とコロイダルシリカを活用した開発品にて塗り材CCT-A620Tの残存線変化率 (Fig.6), 曲げ強度 (Fig.7) を示す。開発品CCT-A620Tはバインダーにコロイダルシリカを使用しているため、加熱処理温度の上昇に伴って強度が増大する特徴を示し、セメントの特徴である1000℃加熱後の強度低下がなく、加熱処理温度変化に伴う強度変化が小さい特徴を有している。

5. 3 耐熱スポーリング性

Fig.8に熱スポーリング試験の概略図、Table 3に試験後試料外観を示す。40×40×40mmの試験片を作製し、1400℃の電気炉内で15分間加熱後、3分間の水冷と12分間の空冷を行い、加熱と冷却を7回繰り返して、亀裂の発生状況を評価した。開発品CCT-A620Tは、従来品にて塗り材と比較して優れた耐熱スポーリング性が認められた。開発品は、加熱処理温度変化に伴う強度および容積変化が小さいことが耐熱スポーリング性向上に寄与したと考える。

CCT-A620T exhibits good workability with sufficient working life.

5. 2 Physical properties

The permanent linear change and modulus of rupture of the newly developed troweling repair material, CCT-A620T, in which colloidal silica is used as binder is compared with that of a conventional cement blended troweling refractory in Fig.6 and Fig.7, respectively. Because of the use of colloidal silica as binder, CCT-A620T exhibits a steady increase of mechanical strength in accordance with elevated heat treatment temperature with no strength reduction at around 1000 °C, which is generally observed in cement blended refractories.

5. 3 Thermal spalling resistance

A schematic diagram of the thermal spalling test is shown in Fig.8. A heating/cooling cycle in which a 40 mm cubic sample specimen was heated at 1400 °C for 15 minutes in an electric furnace and cooled down in water for 3 minutes followed by air cooling for 12 minutes was repeated seven times. After completion of the thermal spalling test, the degree of crack initiation was observed for evaluation. The appearances of the thermal spalling test specimens are comparatively shown in Table3. In comparison with the conventional cement blended troweling refractory, CCT-A620T exhibits superior thermal spalling resistance. It is inferred that smaller fluctuation in mechanical strength and volume change by elevation of heat treatment temperature contributed to the improved thermal spalling resistance of CCT-A620T.

5. 4 Erosion resistance to FeO

A schematic diagram of the erosion test is shown in Fig.9. Mill scale was put in crucible samples made of CCT-A620T and a conventional troweling refractory. Then, the crucible samples with a firmly fixed lid were heated at 1500 °C for 3 hours. After heating, the crucible samples were cut into halves to observe erosion by FeO as well as the FeO penetration depth in the troweling refractories. A cross section of the crucible sample after the erosion test is comparatively shown in Table4. In comparison with the conventional troweling refractory, CCT-A620T exhibits improved erosion resistance to FeO. The chemical and physical characteristics of CCT-A620T and those of a conventional troweling refractory are compared in Table5. Application of colloidal silica as a binder has enabled the advantageous blending design of CCT-A620T so as to increase Al₂O₃ content in association with lowering of CaO component to

[Test conditions]

Test temperature: 1400 °C (heating 15 min-water cooling 3 min-air cooling 12 min) × 7 cycle

Sample shape: 40 × 40 × 40 mm

Evaluation method: Qualitative evaluation based on sample appearance after testing

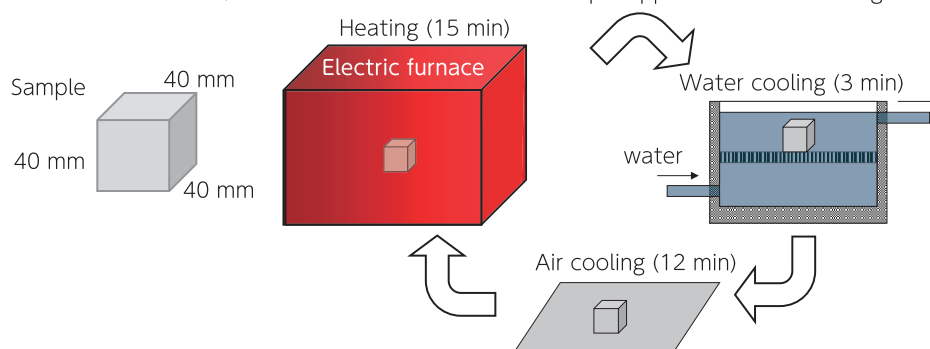


Fig. 8 Schematic diagram of thermal spalling test.

Table 3 Appearance of thermal spalling test specimen

Sample	Conventional	Developed CCT-A620T
Appearance of sample		

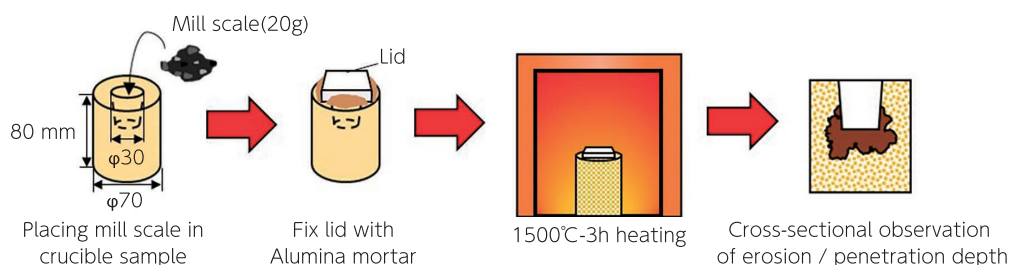


Fig. 9 Schematic diagram of crucible sample erosion test with mill scale.

Table 4 Cross section of crucible sample after erosion test

Sample	Conventional	Developed CCT-A620T
Cross section of crucible sample after erosion test		

Table 5 Typical characteristics of CCT-A620T and conventional troweled refractory

Product		Conventional	Developed CCT-A620T
Chemical composition / %	Al ₂ O ₃	60	70
	SiO ₂	34	27
	CaO	4	0
Linear change / %	110°C-24h	-0.05	-0.18
	1000°C-3h	-0.20	-0.19
	1500°C-3h	-0.71	0.06
Modulus of rupture / MPa	110°C-24h	6.5	2.4
	1000°C-3h	3.2	4.6
	1500°C-3h	20.4	7.7
Binder		Alumina cement	Colloidal silica

5. 4 耐FeO性

Fig.9にるつぼ浸潤試験の試験概略図, Table 4に試験後試料切断面示す。るつぼ形状のサンプルを作製し, 内側にミルスケールを投入して1500℃で3時間加熱後, 試験片を切断して反応状況を比較した。開発品CCT-A620Tは, 従来品こて塗り材と比較して大幅な浸潤抑制効果を得た。Table 5に従来品こて塗り材と開発品CCT-A620Tの品質表を示す。コロイダルシリカをバインダーとして使用することで, CaOレス且つ高 Al_2O_3 組成の配合設計が可能となり, FeOに対する反応性が低下したと考える。

6. まとめ

膨潤性に優れる粘土を適用することで, コロイダルシリカを活用した材料の課題である渴きを抑制し, パッチング施工とこて塗り施工の両方に対応した高耐用スキッドパイプ用補修材CCT-A620Tを開発した。

almost zero (0). It is inferred that the reactivity of CCT-A620T with FeO is lowered by such change in chemical composition.

6. Conclusion

High-durability troweling repair refractory material, CCT-A620T, was developed for the skid pipe in reheating furnace by applying clay with a good swelling property in order to suppress quick drying of the refractory body surface, which is one of the difficult points caused by the use of colloidal silica. CCT-A620T is applicable for both patching and troweling repair work.

Reference

- 1) S. Komori, K. Komatsubara and S. Suetake: Shinagawa Technical Report, **66** 16-29 (2023).