

SHINAGAWA TECHNICAL REPORT

新規ロングノズル浸漬部材の開発

Development of New Immersion Part Materials
for Ladle Shrouds

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品川技報

製品紹介 PRODUCTS

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要 旨

ロングノズル浸漬部の割れ対策として、材質の耐熱衝撃性や品質変化抑制が挙げられる。当社では、黒鉛粒度構成を最適化することで高い耐熱衝撃性を有する材質を開発した。本報告では、新規ロングノズル浸漬部材とその実績を紹介する。

Abstract

Improving thermal shock resistance and suppressing quality deterioration during use are countermeasures for preventing cracking failure at the immersion area of the ladle shroud. We have developed materials with high thermal shock resistance by optimizing the graphite grain size distribution. In this report, we introduce a new ladle shroud immersion part material and its actual results.

1. 緒言

連続 casting におけるロングノズル（レードルシュラウド：Ladle shroud）は取鍋からタンディッシュ（TD）へ溶鋼を注入するための耐火物であり、溶鋼が外気と接しないようにすることで溶鋼の再酸化を防止する役割を担っている。ロングノズルの損傷形態には下部欠損や折損、縦亀裂といったものが挙げられる。Fig.1にA製鉄所におけるロングノズルの損傷要因を示す。下部欠損や縦亀裂が大半を占めており、このような浸漬部の損傷を回避することが重要である。ここで、Fig.2にB製鉄所における浸漬部の損傷タイミングを示す。損傷は加熱冷却を繰り返した casting 後半で発生

1. Introduction

A ladle shroud in continuous-casting is a refractory used for introducing molten steel from a ladle into a tundish (TD), and prevents re-oxidation of the molten steel by preventing the molten steel from coming into contact with the outside air. The damage forms of the ladle shroud include lower part breakage, fracture, and longitudinal cracks. Figure 1 shows damage form of the ladle shroud at Steelworks A. Lower part breakage and longitudinal cracks are dominant, and it is important to avoid such damage to the immersed part. Figure 2 shows

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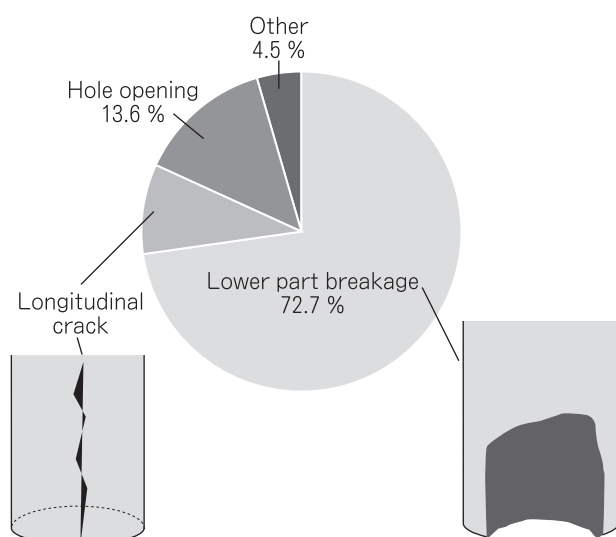


Fig. 1 Types of damage occurring at immersed section of ladle shroud at Steelworks A.

する傾向が認められるので、多チャンス使用に対しても高い耐熱衝撃性を維持できる材質が有効であると言える。

したがって、浸漬部材の耐熱衝撃性や品質変化抑制を目的として従来の汎用浸漬部材の黒鉛粒度構成を最適化することにより高い耐熱衝撃性を有する材質G37S3及びG31S10を開発した。

2. 新規ロングノズル浸漬部材の特性

新たに開発した浸漬部材は、従来の高カーボンノンシリカAG材をベースにその黒鉛粒度構成を最適化した材質である。各種材質の試作焼成品の品質をTable 1に示す。

Fig.3に繰り返し加熱に伴う耐熱衝撃性指数の変化を示す。再加熱試験は1550℃、3 h、N₂雰囲気で行った。侵食試験は溶銑浸漬法で1550℃、1 hの条件で行い、侵食材にはTDフラックス (SiO₂ : Al₂O₃ : CaO = 20 : 20 : 60) を用いて炭酸リチウムで粘度調整した。侵食試験後のベース材質の溶損量を100として耐食性指数を算出した。酸化試験は炉床回転電気炉を用いて、1400℃、1 hの条件で行った。酸化試験後のベース材質の平均酸化層厚みを100として、耐酸化性指数を算出した。

新規材質は試作焼成品においても繰り返し加

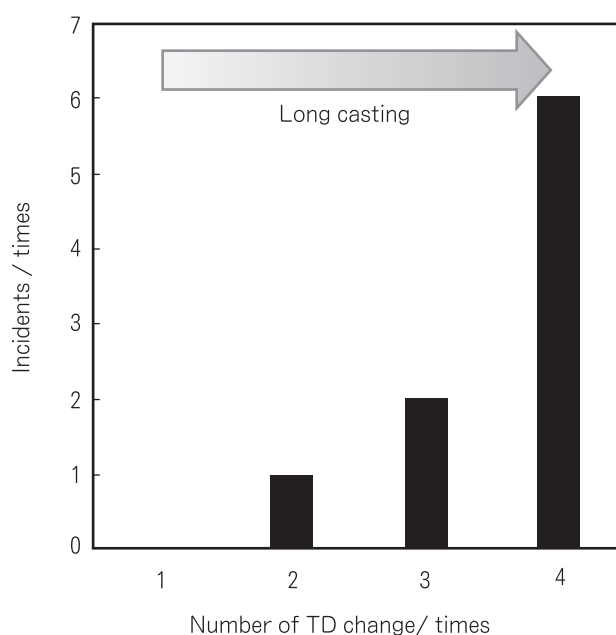


Fig. 2 Timing of damage occurring at immersed section of ladle shroud at Steelworks B.

the timing of the occurrence of the damage to the immersed part in Steelworks B. Since the damage tends to occur in the latter half of casting when heating and cooling are repeated, material capable of maintaining high thermal shock resistance is considered to be effective, even for use with multiple TD changes.

We have developed new materials G37S3 and G31S10, which have excellent thermal shock resistance, by optimizing the grain size distribution of the graphite material in order to suppress deterioration of thermal shock resistance and property changes during use.

2. Characteristics of the New Immersion Part Materials for Ladle Shroud

The newly developed immersion material has optimized graphite particle size distribution based on conventional high carbon non-silica AG material. Table 1 shows the qualities of some prototype products.

Figure 3 shows the thermal shock resistance

Table 1 Properties of newly developed products

		Base	1	2	3
Chemical composition / %	Al ₂ O ₃	62	62	62	68
	C+SiC	37	37	37	31
	C material size (median)	coarse	medium	fine	fine
Apparent porosity / %		13.3	16.4	17.1	15.9
Bulk density		2.54	2.51	2.42	2.49
Modulus of rupture / MPa		11.1	10.8	10.7	13.5
Coefficient of thermal expansion at 1000 °C / K ⁻¹		0.42	0.38	0.35	0.37
Thermal shock resistance index R [*]		100	113	149	157
Corrosion resistance index		100	98	94	101
Oxidation resistance index		100	98	94	89

※R=S/(Eα) S: Modulus of rupture / MPa, E: Modulus of elasticity / GPa,
α: Coefficient of thermal expansion / K⁻¹

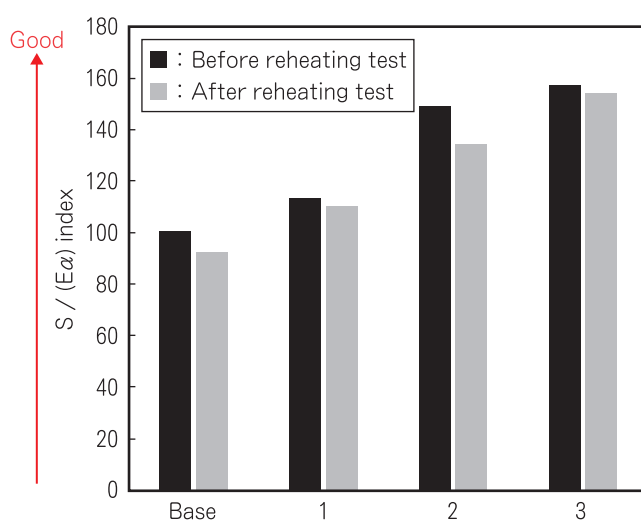


Fig. 3 Change in S/(Eα) index with repeated heating.

熱後においてもベース材質より高い耐熱衝撃性を示した。また、No.1よりも黒鉛が細かいNo.2及びNo.3はさらに高い耐熱衝撃性を示した。侵食試験及び酸化試験の結果、Total黒鉛量が同じであるNo.1及びNo.2はベース材質よりも高气孔率であり、耐食性及び耐酸化性がやや劣る傾向が認められたが、その差は軽微であった。一方で、Total黒鉛量を減らしたNo.3は耐食性がベース材質と同等であった。実機での使用後の結果も踏まえて、耐食性及び耐酸化性に難があるかどうかの見極めは必要である。

index change with repeated heating. The reheat test was conducted at 1550 °C for 3 hours in a N₂ atmosphere. The erosion test was carried out at 1550 °C for 1 hour by immersion method¹⁾. The erosion material was TD-flux (SiO₂: Al₂O₃: CaO = 20:20:60) with lithium carbonate, which was added in order to adjust viscosity. The corrosion resistance index of the base material after the erosion test was calculated as 100. The oxidation test was conducted using a rotary hearth electric furnace at 1400 °C for 1 hour. The oxidation resistance index was calculated by setting the average oxide layer thickness of the base material after the oxidation test to 100.

The new material exhibited higher thermal shock resistance than the base material both in the prototype fired product and after repeated heatings. In addition, No.2 and No.3, which were finer in graphite than No.1, exhibited higher thermal shock resistance. As a result of the erosion test and the oxidation test, No.1 and No.2, which had the same total graphite content, had higher porosity than the base material, and tended to have slightly inferior corrosion resistance and oxidation resistance, but the differences were slight. On the other hand, No.3,

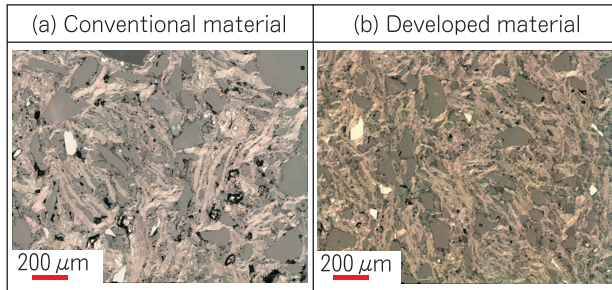


Fig. 4 Micrographs of each material.
(a)Conventional and (b)Developed

新規材質の組織写真をFig.4に示す。新規材質の組織はベース材質に比べると黒鉛原料がアルミナ粒子間に入り込んだような組織をしていた。

Table 2に新規材質G37S3とG31S10の代表品質を示す。

3. 実機適用実績

B製鉄所の連続鋳造機において新規材質を浸漬部に適用したロングノズルが使用された。B製鉄所での使用後品の浸漬部 S/E（S：曲げ強度，E：弾性率）をFig.5に示す。

いずれの使用後品も品質に異常は認められず、

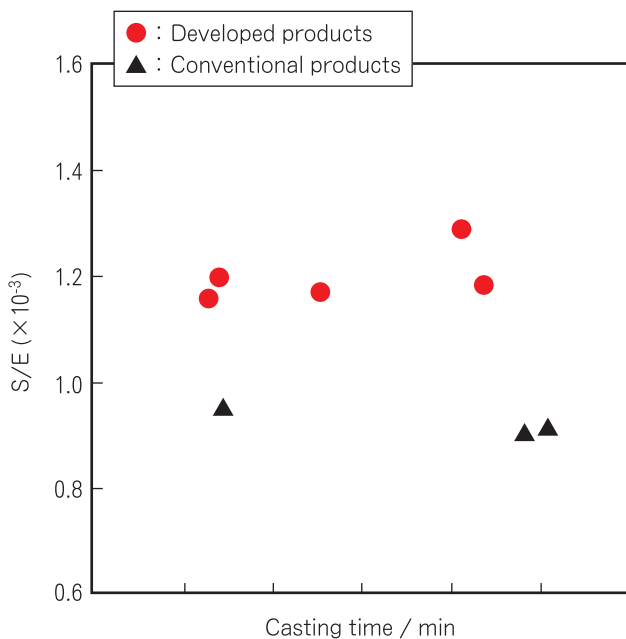


Fig. 5 Results of S/E of used ladle shrouds at Steelworks B.

Table 2 Typical properties of newly developed products

		G37S3	G31S10
Chemical composition / %	Al ₂ O ₃	62	68
	C + SiC	37	31
Apparent porosity / %		16.5	16.0
Bulk specific gravity		2.50	2.50
Modulus of rupture / MPa		11.0	13.5

in which the quantity of total graphites was reduced, had the same corrosion resistance as that of the base material. Based on the results after use in actual machines, it was concluded that it was necessary to determine whether the slight deterioration in corrosion resistance and oxidation resistance is critical or not.

Figure 4 shows the microstructure of the developed material. Compared with the base material, the structure of the new material was such that the graphite raw material were distributed evenly among the alumina particles.

Table 2 shows the typical properties of G37S3 and G31S10.

3. Actual Application Results

In the continuous casting machine of the Steelworks B, the ladle shroud in which a new material was applied to the immersion part was used. The S/E (S: Modulus of rupture, E: Modulus of elasticity) of the immersed part after use at Steelworks B is shown in Fig. 5.

No abnormality was observed in the quality of any of the products after use, and the S/E tended to be higher than that of the products after use of the conventional materials in the past.

The new material, having the optimized graphite grain size distribution, has high thermal shock resistance at the manufacturing

過去の従来材使用後品に比べてもS/Eが高い傾向が認められた。

黒鉛粒度構成を最適化した新規材質は製品段階で高い耐熱衝撃性を有しており、繰り返し加熱が行われるようなロングノズルの浸漬部材として有用である。今後、各所での安定使用に期待できる。

stage, and is useful as an immersion part material of a ladle shroud in which repeated heating is performed. The developed material can be expected to function stably in various plants.

Reference

- 1) H. Niitsuma, K. Moriwaki and W. Lin : Shinagawa Technical Report, [57] 49-60 (2014).