

SHINAGAWA TECHNICAL REPORT

API鋼種向けの塩基性SVプレート“SVR-FB9”

Basic Refractory SV Plate “SVR-FB9” for
Ca-treated API Steel Grades

馬 場 浩 樹
Hiroki BABA

犬 飼 恵 輔
Keisuke INUKAI

濱 本 直 秀
Naohide HAMAMOTO

新 妻 宏 泰
Hiroyasu NIITSUMA



製品紹介/PRODUCT

API鋼種向けの塩基性SVプレート“SVR-FB9”

Basic Refractory SV Plate “SVR-FB9” for Ca-treated API Steel Grades

馬 場 浩 樹 ^{*1}	犬 飼 恵 輔 ^{*2}
Hiroki BABA	Keisuke INUKAI
濱 本 直 秀 ^{*3}	新 妻 宏 泰 ^{*4}
Naohide HAMAMOTO	Hiroyasu NIITSUMA

要 旨

溶損鋼種(API鋼)用の取鍋プレートは損傷の大きい部位(孔周囲と摺動範囲)にCa成分に対して耐食性の高い ZrO_2 材質を配材した ZrO_2 材質アセンブリ型プレートが適用されている。しかし、このアセンブリ型プレートは焼き付きや酸素洗浄による損傷に加えて、アセンブリ型プレート特有の現象である ZrO_2 材質部の脱落が起こり易いという問題がある。今回開発した塩基性SVプレート“SVR-FB9”はカーボン含有した塩基性プレートで、焼き付き損傷が抑制され、酸素洗浄にも強い材質である。また、従来材より強度を付与したことで孔径の大きな大型形状プレートへの適用が可能で、アセンブリを必要としない一体構造のAPI鋼種向けSVプレートである。この開発したSVプレートは、突発な鑄造計画変更に対してもフレキシブルに対応でき一般鋼用との併用に期待が持てる。

Abstract

For steelmaking of Ca-treated API steel grades, two component SV plate in which a small piece of ZrO_2 plate with superior corrosion resistance to Ca component is inserted at the critically damaged area (central bore and major sliding area) of Al_2O_3-C SV plates. However, difficulties such as localized damages on the ZrO_2 plates by sticking or FeO corrosion caused by oxygen gas cleaning as well as exfoliation of the ZrO_2 plates out of the base Al_2O_3-C SV plate during inspection/repair work with full-opening of SV mechanism accompany such two component SV plates. In this regard, new basic refractory SV plate material, SVR-FB9, is developed. Sticking damage is suppressed through the addition of carbon in SVR-FB9, and its basicity also gives it sufficient durability against oxygen gas cleaning. SVR-FB9 implements enhanced corrosion resistance to Ca-treated API steel grades as well as improved strength, so it is applicable for large-sized single material SV plates, so it is expected that, because of the compatibility of SVR-FB9 plate to the Al_2O_3-C SV plate commonly applied for general steel grades, coped with sudden schedule changes in the steelmaking process will be more easily.

1. 緒言

スライドバルブプレート(以下SVプレート)に使用される材質としては耐スポール性と耐食性のバランスが取れた

1. Introduction

Because of well-balanced spalling and corrosion resistance, Al_2O_3-C refractories are commonly

*1 技術研究所 第3研究部 第1研究室 Flow Control Refractories R&D Sec., Research Dept. No.3, Research Center

*2 岡山工場 第3製造室 主任部員 Staff Manager, Production Sec. No.3., Okayama Plant

*3 技術研究所 第3研究部 第1研究室 主任研究員 Senior Researcher, Flow Control Refractories R&D Sec., Research Dept. No.3, Research Center

*4 技術研究所 第3研究部 第1研究室 室長 Chief Manager, Flow Control Refractories R&D Sec., Research Dept. No.3, Research Center

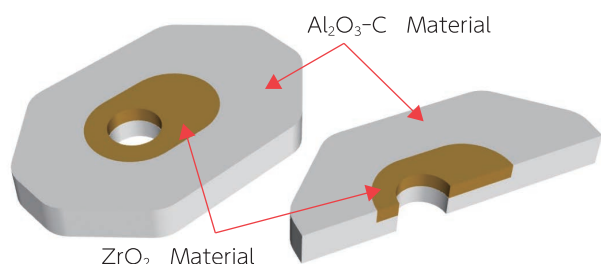


Fig. 1 Schematic illustration of two component SV plate.

$\text{Al}_2\text{O}_3\text{-C}$ 材質が一般的であるが、原油、天然ガス向けラインパイプ用鋼種（以下API鋼）の casting においては、その高い鋼中Ca成分に起因した溶損が問題となり適用が難しい¹⁾。そのため、従来API鋼向けプレートにはCa成分に対する高い耐食性を特長とする ZrO_2 材質が適用されてきた。その際、 ZrO_2 材質は高密度なために製品重量が大きくなることや、温度変化に伴う体積変化が大きいなどの理由により、大型プレートへの適用に際してはFig.1のように本体部に汎用的な $\text{Al}_2\text{O}_3\text{-C}$ 材質を配材し、 ZrO_2 材質は溶鋼と接する摺動面と孔回りにのみに耐火モルタルを用いて固定したアセンブリ型プレートが適用されてきた。一方でこの ZrO_2 材質アセンブリ型プレートでは、プレート製造時のアセンブリ工程付加に伴う製造負荷増に加え、プレート使用時においても①焼き付き剥がれ損傷発生に伴うプレート解放点検時の内挿 ZrO_2 材質プレートの本体からの脱落や、② ZrO_2 材質が FeO に対する耐食性が低位であることより、酸素洗浄や使用中の吸気に起因した FeO による異常溶損等の問題が発生する場合がある。また、 ZrO_2 材質アセンブリ型プレートはAPI鋼種専用として使い分けされていることが多く、突然の casting 計画変更に従従し難い面もある。これらのAPI鋼向け ZrO_2 材質アセンブリ型プレートでの問題回避のため、 ZrO_2 材質と同じくCa成分に対する高い耐食性を具備した塩基性材質での大型プレート一体材質化についての検討を行った。

これまでに当社では、塩基性材質の耐スポール性を改善することにより多数回使用可能なSVR-FB8を開発し、実機にて良好な結果を得ている²⁾。ただし、同材質はやや低強度であり、大きな外力が負荷された状態で使用される大型形状のプレート用途には適さない。さらに大型形状プレートでは、プレート使用時の孔周囲と外周部での温度ギャップによる熱スポールが問題となる場合があり、塩基性材質の大型形状プレートへの適用には更なる耐スポール性の向上も求められる。そこで塩基性材質で一体物大型形状プレートへの適用を目指し、SVR-FB8よりも更に高強度、高耐熱

applied for the slide valve plate (hereinafter referred to as “SV plate”) mounted onto the steel ladle or tundish for continuous casting. In the steelmaking process of Ca-treated API steel grades, which are adopted for crude petroleum or natural gas steel pipe products, however, use of $\text{Al}_2\text{O}_3\text{-C}$ type SV plate is inadequate because of severe corrosion by the Ca component contained in molten steel¹⁾. For this reason, ZrO_2 which is, characterized by superior corrosion resistance to Ca component has been adopted for the steelmaking of Ca-treated API steel grades. Since the high density ZrO_2 material makes the product weight heavier and the volume changes greatly with temperature, ZrO_2 material is locally applied in two component SV plate, especially, for large-sized SV plates for the steel ladle. That is, as schematically illustrated in Fig. 1, a small piece of ZrO_2 plate is inserted in the central area of the $\text{Al}_2\text{O}_3\text{-C}$ SV plate with refractory mortar so that it covers the area that is critically damaged where molten steel contacts directly. The following difficulties accompany to two component SV plate in its production process as well as in several scenes of practical steelmaking operation; (1) The manufacturing load is increased by additional process of assembling work. (2) The inserted ZrO_2 plate piece tends to be exfoliated from base $\text{Al}_2\text{O}_3\text{-C}$ SV plate when inspection/repair work is carried out on SV plates which are damaged by sticking and peeling during full-opening of the SV mechanism. (3) Due to the inferior corrosion resistance of ZrO_2 to the FeO component, ZrO_2 plate is corroded by the FeO generated by oxygen gas cleaning of the SV plate or by the reaction between molten steel and sucked air. (4) Since SV plate with the inserted ZrO_2 component plate is exclusively used for Ca-treated API steel grade, sudden schedule changes in steelmaking process may cause difficulties. To avoid difficulties caused by ZrO_2 component containing two component SV plate, a large-sized single material SV plate made of basic refractory with high corrosion resistance to Ca component needs to be developed.

We have been developing a basic refractory SV plate, with improved spalling resistance, called SVR-FB8, which can be used for multiple heats

スポール性化を図った材質SVR-FB9を開発した。本報では、SVR-FB9の特徴について紹介する。

2. SVR-FB9の特徴

SVR-FB9は①骨材にスピネルを適用、②従来の塩基性材質よりも高温での焼成、③粒度構成の最適化の3種の手法により高強度並びに耐スポール性の向上を図った材質である。本稿では、SVR-FB9の(1)品質特性、(2)耐スポール性、(3)耐食性の評価結果を示す。

2.1 品質特性

Table 1にSVR-FB9の代表品質表を、Fig.2に曲げ強度指数を示す。SVR-FB9は、従来の塩基性材質であるSVR-FB8と比較して曲げ強度が約3倍に向上した。これは大型形状プレートが使用時に付加される大きな外力にも耐えられる高強度である。

2.2 耐スポール性の評価試験

SVR-FB9の耐スポール性を溶銑浸漬スポーリング試験で評価した。試験は35mm角柱状に加工したサンプルを1600℃の溶銑に1分間浸漬させ、その後自然空冷した。試験後試料は亀裂部を樹脂含浸により補強した状態で切断

Table 1 Typical properties of SVR-FB9 and SVR-FB8

Brand name	SVR-FB8	SVR-FB9
Quality	MgO-Spinel-C	Spinel-C
Chemical composition / mass%		
MgO	50	20
Al ₂ O ₃	38	70
C	6	4
Metal	$\alpha + \beta$	β
Apparent porosity / %	9	10.5
Bulk density / kg·m ⁻³	2990	2950
Cold crushing strength / MPa	105	130

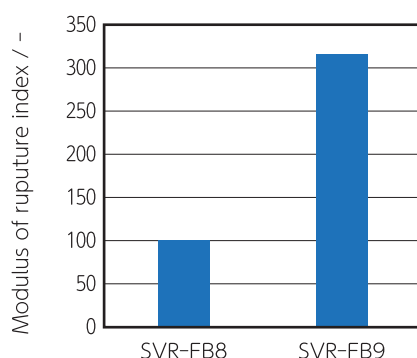


Fig. 2 Comparison of modulus of rupture (index) between SVR-FB8 and SVR-FB9.

with satisfactory performances in actual continuous casting operations²⁾. Because of relatively low mechanical strength, however, it is thought not to be usual for large-size SV plates, onto which large external force is loaded. In addition, since thermal spalling can be induced by large differences in temperature between the central bore area and outer peripheral in large-sized SV plates, further improvement of spalling resistance was necessitated. In order to put large-sized single material basic refractory SV plate into actual usage, a new basic refractory material for SV plate, SVR-FB9, with better mechanical strength and spalling resistance than those of SVR-FB8, was developed. The major characteristics of SVR-FB9 are introduced in this article.

2. Characteristics of SVR-FB9

Newly developed basic refractory material for SV plate, SVR-FB9, is characterized by high mechanical strength and greatly improved spalling resistance, which was realized by (1) adoption of aggregate spinel raw material, (2) firing at higher temperature than the conventional firing temperature for basic refractory materials, and (3) optimization of particle size distribution. The major properties of SVR-FB9 are described along with spalling and corrosion resistance results in the following sub-sections.

2.1 Physical properties

The typical properties of SVR-FB9 compared with those of SVR-FB8 are shown in Table 1. As shown in Fig. 2, in which the modulus of rupture of SVR-FB9 is compared with that of SVR-FB8, the bending strength of SVR-FB9 has been increased almost 3 times that of SVR-FB8's. The attained mechanical strength of SVR-FB9 is sufficient to endure the large external force loaded onto large-sized SV plates.

2.2 Evaluation of spalling resistance

The spalling resistance of SVR-FB9 was evaluated along with SVR-FB8 and Al₂O₃-C material commonly applied for SV plate using hot metal dipping method. Rectangular spalling test specimens with 35 mm square base face were dipped into hot metal kept at 1600 °C for 1 minute, followed by air cooling. After reinforcing the crack-initiated portions by impregnating resin, test specimens were cut into

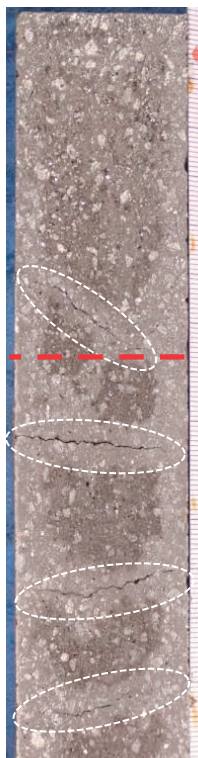
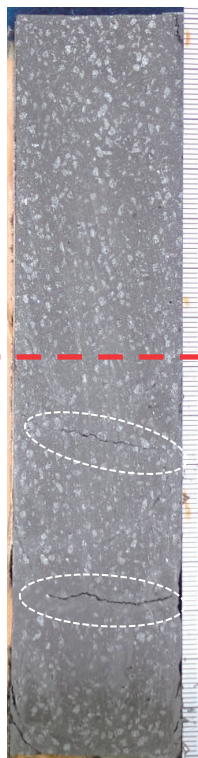
	SVR-FB8	SVR-FB9	Al ₂ O ₃ -C
Cross section			
Number of cracks / lines	4	2	2

Fig. 3 Cross section of spalling test specimens.

加工し、切断面の亀裂本数で評価を行った。試験後試料の切断面写真をFig.3に示す。比較試料のSVR-FB8では、試験時湯面位置 (Fig.3赤点線部) 付近に発生した亀裂を含め亀裂発生本数は4本であるのに対して、SVR-FB9では亀裂発生本数は2本に半減し、一般鋼用のAl₂O₃-C材質と同程度であった。この結果より、SVR-FB9では耐スポール性の向上により大型プレートで発生しやすい孔周りの熱スポール亀裂が低減でき、一般鋼用のAl₂O₃-C材質と同程度の耐用が期待できる。

2. 3 耐食性評価試験

SVR-FB9はSVR-FB8と比較してMgO比率が低減されている。一般的に塩基性材質においてFig.4のようにMgO比率を減少させると耐食性を低下させることが知られている³⁾。そのため、SVR-FB9では粒度構成を最適化することで耐食性の改善を行った。

耐食性はFig.5に示す回転るつば侵食試験によって評価した。試験は、CaO-Al₂O₃-SiO₂-FeO系の合成スラグを使用し、1650℃-5h (1h毎にスラグ交換) の条件で行った。

halves to evaluate their cross sections. The cross sections of the halved spalling test specimens are comparatively shown in Fig. 3, in which the red color dotted line indicates the hot metal bath surface. SVR-FB8 exhibits four initiated cracks in the cross section, one at vicinity of the hot metal bath surface and three in the hot metal bath. While, only two initiated cracks are observed on the SVR-FB9 cross section, which is equivalent to Al₂O₃-C material, which is commonly applied for SV plate. It can be concluded from the spalling test results that the improved spalling resistance of SVR-FB9 reduces thermal spalling cracks around bore that tend to occur in large-sized SV plates. It is expected to have a durability equivalent to that of Al₂O₃-C materials for general steel.

2. 3 Evaluation of corrosion resistance

In comparison with SVR-FB8, the percentage of MgO in SVR-FB9 has been lowered to secure spalling

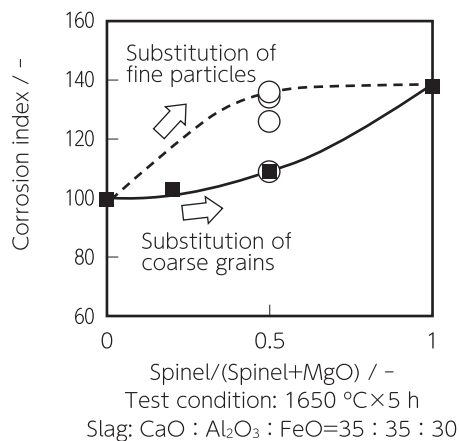


Fig. 4 Influences of MgO content in MgO-spinel system and spinel grain size on corrosion resistance of basic refractory³⁾.

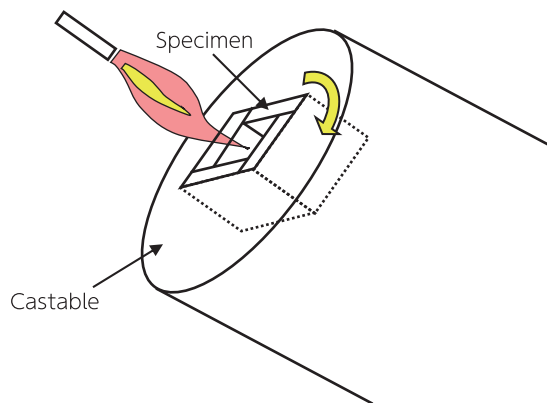


Fig. 5 Schematic illustration of rotary crucible corrosion test.

resistance so as to be applicable to large-sized SV plates. It is known as indicated in Fig. 4, that the corrosion resistance of basic refractories is lowered in accordance with lowering the MgO fraction in MgO-spinel system³⁾. It should be noted that the degree of deterioration of corrosion resistance by lowering MgO component is greatly influenced by substituted spinel particle size, namely, less deterioration occurs with substitution of aggregate spinel particles for fine spinel particles. Referring to such knowledge, the raw material blend design of SVR-FB9 was created by adopting aggregate spinel material and optimizing particle size distribution.

Corrosion resistance of SVR-FB9 was evaluated by rotary crucible corrosion test. The schematic illustration is shown in Fig. 5. The corrosion test was conducted at 1650 °C for 5 hours with CaO-Al₂O₃-SiO₂-FeO synthetic slag, which was exchanged every hour. Cross section of corrosion test specimen of SVR-FB9 compared with SVR-FB8 is shown in Fig. 6 along with corrosion resistance which was calculated from the corroded depth of test specimen. In comparison with SVR-FB8, the corrosion resistance of SVR-FB9 was improved by roughly 25 %. It is inferred that the corrosion resistance of SVR-FB9 is sufficient for application to steelmaking of Ca-treated API steel grades.

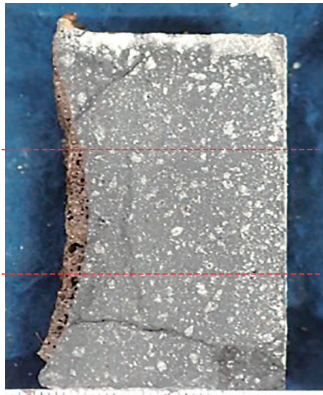
	SVR-FB8	SVR-FB9
Cross section		
Corrosion resistance index / -	100	76

Fig. 6 Cross section of corrosion test specimen and calculated corrosion resistance.

Fig.6に試験後試料の切断面写真および溶損量より算出した溶損指数を示す。SVR-FB9はSVR-FB8と比較し約25%の耐食性向上が認められた。この結果よりSVR-FB9はAPI鋼種用プレートとして適した高い耐食性をもつと考えられる。

3. まとめ

本報では塩基性プレート材質として高強度、高耐スポール性を特長とするSVR-FB9を紹介した。SVR-FB9はその品質特性より、 ZrO_2 材質アセンブリ型プレートに替わってAPI鋼種用として一体構造の大型プレートへの適用が可能であり、また、突発な鑄造計画変更に対してもフレキシブルに対応でき一般鋼用との併用に期待が持てる。

3. Conclusion

A new basic refractory SV plate material, SVR-FB9, with improved corrosion resistance and sufficient spalling resistance to be applicable for large-sized SV plate has been developed. To be used in place of the ZrO_2 piece inserted in two component SV plate, which has been used for Ca-treated API steel grades. It is expected that SVR-FB9 single material plate, is adequate to be used for steelmaking of Ca-treated API steel grades with compatibility to the Al_2O_3 -C SV plate commonly used for general steel grades. It will also permit sudden schedule changes in the steelmaking process with little trouble.

References

- 1) T. Sugino, K. Hayami and T. Kawamura: TAIKABUTSU, **44** 263 (1992).
- 2) N. Hamamoto, H. Baba, T. Matsunaga and T. Horiuchi: Shinagawa Technical Report, **66** 42-49 (2023).
- 3) F. Mizobuchi, N. Hamamoto and K. Moriwaki: Shinagawa Technical Report, **60** 69-77 (2017).